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PREFACE (MS and MT)

Martin (MS) and I (MT) have been encouraged to write this volume of *Geochemical Perspectives* in a travelogue style, sketching out the research terrain we entered and encountered as post-graduates, and then relating why we tackled particular problems in the order we did. We have been encouraged to acknowledge the wisdom of our mentors, peers, post-docs and post-graduates along the journey, which has been a great pleasure. We feel we are nowhere near our final destination as yet - there are paradigm shifts occurring in the field of glacier biogeochemistry even as we write – and we hope that this is a stimulus for early career researchers who may read this manuscript. We further hope that the story of the origins of the study of glacier biogeochemistry that we narrate will capture your imagination, as it did ours, and that we can convince you that glaciers and ice sheets are important and dynamic components of the Earth system.

Neither of us imagined that we would have a research career in glaciology that would involve such a major role for microbially-mediated processes in what were once thought to be biologically inert environments, even as recently as the 1980's. It would be hard to contend that we had a master plan for getting to tenured faculty positions when we were Ph.D. students. We confess to be only curiosity-driven and –led scientists, and not grand strategists. I'll hand over to the other Martin, who is more glaciological than me, to relate how he became interested in glacier hydrology and hydrochemistry. I'll return later with how I got hooked on the subject, and how we came to work together.

Martin Sharp (MS)
Earth and Atmospheric Sciences
University of Alberta
Edmonton, Alberta T6G 2E9, Canada

Martyn Tranter (MT)
School of Geographical Sciences
University of Bristol
Clifton, Bristol BS8 1SS, United Kingdom

ABSTRACT

This volume charts our interlinked research pathways, which began with an interest in water flow paths at glacier beds and expanded into an exploration of the role of glaciers and ice sheets in local, regional, and global biogeochemical cycles. Along the journey, we discovered that glacier beds are habitats for microbes, and that the microbes are sustained by a variety of rock- and organic carbon-related processes. We were encouraged to write our story in a travelogue style, highlighting the contributions of the great students, post docs and colleagues we have had the pleasure to work with, the sometimes random nature of the factors that led us to explore new systems and processes, and some of the dead ends we ran into. We could have written so much more, but we have covered the state of the science when we were post grads, the things that motivated us to study rock dissolution and water flow paths at glacier beds, what happened when we explored glacier beds for the first time, in terms of biogeochemical weathering reactions, our desire to upscale from small valley glaciers to the larger ice masses of Svalbard and Ellesmere Island and, finally, the opportunities we had to work on the biogeochemistry of the Greenland and Antarctic Ice Sheets. It is with some pride that we note that most of the biogeochemical processes we deduced from our studies of smaller glacier systems also occur beneath the large ice masses, given due regard to differences in spatial scale, the timescales on which processes operate, and the provenance of sediment at the glacier beds. Our students have made huge contributions to the field of glacier biogeochemistry, the role of glaciers in fertilising the oceans, and the role of bedrock abrasion and crushing in subsidising microbial communities beneath ice sheet interiors. We suspect that these are going to be topics they will write about in future volumes of this series, as a minimum.

1. INTRODUCTION – HOW WE GOT INTO GLACIER HYDROLOGY AND HYDROCHEMISTRY IN THE 1970's

1.1 First Steps (MS)

I saw my first glacier in Iceland in 1973 on a school field trip. It was the ice cap on top of Snaefell in Iceland – in literature, it is the start of the Jules Verne's Journey to the Centre of the Earth, which, with the benefit of hindsight, seems more prophetic than I imagined at the time (Fig. 1.1). The next year, I had the chance to visit Chamonix, a place that plays an important role in the early annals of glaciology and is site of some of the earliest *in situ* subglacial science – in the tunnel beneath the Glacier d'Argentière. On that visit, I got to explore along the margins of the Glacier des Bossons (Fig. 1.2), and I think I was hooked from that point on.

Figure 1.1 Snaefellsjokull, Iceland – Martin's first glacier, and the starting point for the Journey to the Centre of the Earth.

Figure 1.2 Glacier des Bossons, Chamonix, France, where Martin got hooked on glaciers.

In 1976, I went to Cambridge University to study Geography, and in 1978 I had to produce a thesis for my degree program. This seemed like a good chance to go back to Iceland and spend more time around glaciers. With encouragement from Helgi Björnsson, one of the pioneers of modern glacier hydrology, I surveyed a long profile up the centre of the surge-type glacier, Sylgjujökull, on the west side of the ice cap Vatnajökull, and made a study of the shorelines developed around a former surge-dammed lake.

As it turned out, this set me up for Ph.D. research and, in 1979, I moved to Aberdeen to work with David Sugden and Chalmers Clapperton on “A comparison of the landforms and sedimentary sequences produced by surge-type glaciers in Iceland”. This was a life-changing experience, working with two inspirational people. It also meant another two long field seasons in a country I was coming to love. While I was honeymooning (and working) at the surge-type glacier, Eyjabakkajökull in 1981 (Fig. 1.3), I stumbled (and stumbling will be a recurrent theme in this narrative) on a series of exposures that seemed to show that, during a previous surge, the glacier had moved over extremely wet sediments that had been liquefied by the loading pressure of the advancing glacier. Deformation of those sediments played an important role in landform building and probably also contributed to the motion of the overlying ice (an idea that was just starting to emerge in the literature through the work of Geoffrey Boulton). This

kick-started my fascination with the interactions between glaciers and the water that was trying to drain over, through and beneath them.

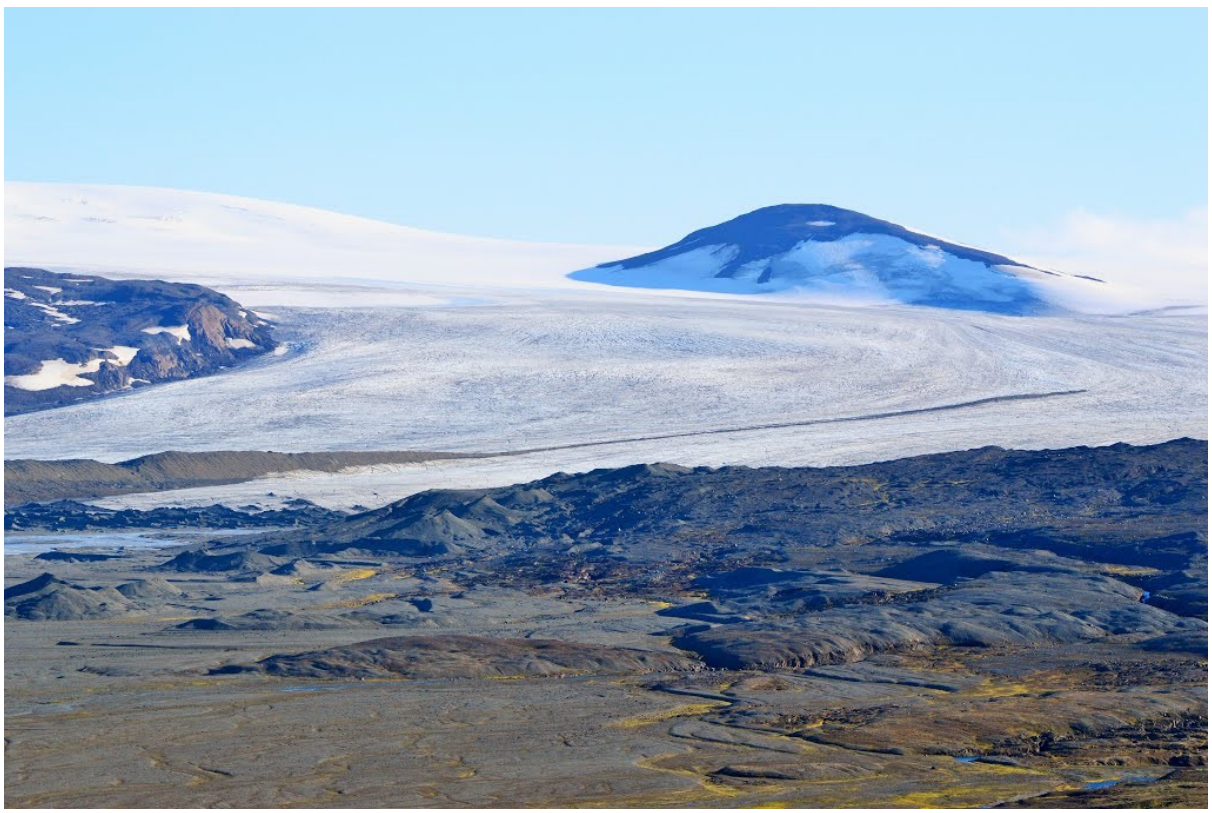

Figure 1.3 Eyjabakkajökull, Iceland, where Martin became convinced that subglacial meltwater and glacier flow are inextricably connected.

1.2 Next Steps – the New World (MS)

After leaving Aberdeen, I was fortunate to win a Junior Research Fellowship at Merton College, Oxford, to study the dynamics of surge-type glaciers. I was even more fortunate that the then Warden, Rex Richards, was willing to give me the freedom to spend significant parts of my Fellowship working elsewhere to develop my knowledge, skills, and experience. This allowed me to spend 6 months at the University of Washington (UW) in Seattle, under the tutelage of Bernard Hallet and Charlie Raymond, who were both great mentors. At the time, UW was an incredibly dynamic environment for anyone interested in glaciers, and many of those I mixed with have gone on to become leaders in their fields – in particular, Bob Anderson, Andrew Fountain, Tad Pfeffer, Joe Walder, Tómas Johannesson and Magnus Magnusson. It has been my pleasure to continue relationships with many of them ever since. The highlight of this first visit to North America was spending the summer of 1983 on Variegated Glacier, near Yakutat in southern Alaska (Fig. 1.4). It was being monitored in the build-up to a surge

that was expected to occur sometime in the mid-1980's – but it conveniently started to surge in the winter of 1982-1983.

Figure 1.4 Alaska's Variegated Glacier during its 1983 surge.

I headed up to Yakutat in early June with Bob Anderson, and found the glacier teeming with activity and famous glaciologists – including Will Harrison, Barclay Kamb, Hermann Engelhardt, Almut Iken, and Keith Echelmeyer – all pioneers of the study of glacier dynamics, glacier hydrology, and *in situ* subglacial investigations. That summer was a key point in my career – working with these people, their students and my UW friends taught me more than I could ever have imagined about how glaciers worked, how people were starting to study them and, most importantly, how much we didn't know. The glacier itself made a big contribution too – almost every day we saw things I don't think any of us ever imagined to be possible – thrust faults forming and then displacing at rates of metres per hour, the glacier thickening at 6 m d^{-1} and more, crevasses forming beneath our feet – the mind was comprehensively boggled! Most important however, from the perspective of this story, was the end of the surge. It happened in a matter of hours – the glacier just stopped moving (having been flowing at 60 m d^{-1} not long beforehand), and released an enormous flood of extremely turbid water. This provided pretty compelling evidence that water storage at the bed was strongly implicated in the glacier's fast flow, and that the surge itself had accomplished a lot of erosion of the glacier's

bed. By this time, there was no way I was going to work on anything other than the interactions between glacier flow, glacier hydrology, and subglacial geomorphological processes. Meltwater chemistry, however, had yet to trouble my consciousness.

1.3 Back to Cambridge (MS)

While on the glacier, I received a message from Bernard Hallet that there was a faculty position in Physical Geography available at Cambridge University and that I was encouraged to apply for it. Barclay agreed that if I produced a CV he would take it with him when he left the glacier and send it to Cambridge for me. It was nearing the end of the season, field books were more or less full, and personal computers had yet to be invented, so I hand wrote my CV on the inside of a breakfast cereal box. Barclay didn't bat an eyelid, and somehow the CV found its way to Dick Chorley in Cambridge (whether still on the cereal box or not I never found out, though Dick would probably have appreciated it all the more if it had been!). When I returned to the UK, I was called for interview and was extremely lucky to be offered the job. I returned to Cambridge in April 1984.

That summer I went back to Seattle to work with Bob Anderson and write up the work we had done at Variegated Glacier the previous summer. As an aside, Bernard sent Bob and I on a mission to Glacier National Park, Montana, to retrieve a time-lapse camera and data logger that he and Joe Walder had installed in a cavity beneath the Grinnell Glacier (Fig. 1.5). For the first time, I realised that (a) it was possible to crawl long distances under some glaciers, and (b) you could do science under glaciers without the benefit of hydro-electricity tunnels or hot water drills. I also learned that there are better ways to download a data logger than spending 9 hours in the dark at 0 °C transcribing each individual data point collected in the previous 2 years into a notebook! We had planned to just pick up the logger and bring it back to Seattle for downloading – but it turned out that with this early model, disconnecting it from its power source would wipe the memory, so we did what we had to do! After escaping from Grinnell, we paid a visit to Blackfoot Glacier, where Bernard and Joe Walder had mapped, in great detail, the geomorphological evidence for patterns of subglacial water flow across the limestone bedrock now exposed in front of the glacier. This included evidence for extensive dissolution weathering of the limestone and for subglacial carbonate precipitation on the downstream side of bedrock bumps – low pressure locations when ice-covered - where water was expected to freeze, thereby concentrating the solute to the point of supersaturation and precipitation. This is where I finally got the message that there might be such a thing as glacier geochemistry and that it might, in some way, be connected to glacier hydrology.

Figure 1.5 Grinnell Glacier, Montana. Early (1984) subglacial exploration with Bob Anderson.

Back in Cambridge, it was time to start a field research programme. By chance, there was another new appointment in the department – Keith Richards, not a guitarist, but a well-known fluvial geomorphologist, who was also looking for ideas for a field programme that we could use as a basis for training students (in those days Cambridge students got very little field training). We decided to pool our resources and settled on the Hardanger ice cap in southern Norway as a suitable field site – where we worked from 1985-1988. This is how I finally got into glacier hydrology. Ian Willis joined us as a Ph.D. student to work there and has now been involved in the field for nearly 30 years (as has one of the undergraduates on that first trip; Peter Nienow). Probably the most important outcome of the work in Norway was that we learned how to conduct dye-tracing experiments on glaciers – our first venture into investigating how the efficiency of glacier drainage systems changes over the course of a melt season. The problem with summers in southern Norway, however, is that it rains a lot. Rain wasn't very compatible with early 1980's era surveying equipment or data loggers, so it was hard to generate long, unbroken series of measurements. At the end of the 1987 field season,

Keith symbolically set fire to his field boots and sent them to a Viking burial in the Hardanger Fjord.

1.4 The Alps (MS)

Our thoughts turned to warmer climes and, in 1988, we decided to try to get funding for a glacier hydrological project in the Swiss Alps. We teamed up with Mike Clark and Angela Gurnell at Southampton University, who had been working in the Arolla Region and had just edited a seminal book “Glacio-fluvial Sediment Transfer: an Alpine Perspective”. It presented what was then the state of the art in the science of glacier hydrology and fluvio-glacial sediment transport, but didn’t say too much about glacier hydrochemistry – which was a fair reflection of the state-of-the-science at the time - although it did contain a chapter on current thinking by Roland Souchez and Reggie Lorrain from Brussels. It was at a meeting to plan the proposal writing for this project that my life path collided with that of the more entertaining Martyn, who had recently taken up a position as a marine sedimentary geochemist in the Department of Oceanography at Southampton. I’ll let him take it from there!

1.5 First Encounters with Glacier Meltwater Geochemistry (MT)

In contrast to Martin, I had no interest in glaciers at all when I embarked on my undergraduate degree in Environmental Sciences at the University of East Anglia (UEA). I didn’t even know that my beloved South Wales Valleys were carved by glaciers, and neither did I want to leave my home in the valleys and go to University. I was happy working with my father in his fruit, veg, and flower shop, and playing cricket for Ebbw Vale. However, both Mam and Dad were keen for me to go to university, and they encouraged me to spread my wings, mix metaphors and sail to the distant flat lands of Norfolk to attend the University of East Anglia (UEA).

I can’t explain why I got interested in silicate rock dissolution, particularly since silicate rocks dissolve in water very slowly, but I did. I’ve always liked puzzles and problems, and there was controversy about what stopped them dissolving more quickly. I got hung up on why one of the most common silicate minerals, feldspar, dissolves in the way it does. Feldspar surfaces initially react rapidly with water, a process known as hydrolysis, but dissolution slows down drastically thereafter. The positively charged cations in the mineral surface, such as Na^+, K^+ and Ca^{2+}, are displaced by H^+, and leave behind a leached surface layer. The controversy in the 1970’s was about the thickness and composition of the leached layer (or indeed whether it existed), and I was hooked on doing my own simple experiments to make a contribution to the debate.

Rob Raiswell (the co-author of the very first *Geochemical Perspectives* issue) taught the Year 2 Geochemistry course, was interested in this general area too, and went on to supervise my undergraduate dissertation on feldspar dissolution in distilled water in free contact with the atmosphere. Peter Brimblecombe taught me Year 3 Environmental Aquatic Chemistry. They were inspirational lecturers and great researchers. I learnt tons about CO_2 and dissolved carbonate species, about pH measurement and the partial pressure of CO_2 in solution, and I learnt lots about solution geochemistry. Rob was becoming interested in glacier hydrochemistry and had a Ph.D. on offer, which included an investigation of silicate dissolution at glacier beds. There was fieldwork in the Alps. I thought that this sounded great fun, and applied for the position. I was very lucky to get the studentship, and was not a good post-graduate. I loved playing cricket and all the socialising that went with it.

Thankfully, Rob was determined to keep me on track, and largely drove me through the Ph.D., despite my kicks, screams and hedonism. He arranged my first field season in the summer of 1979 in the Swiss Alps at Gornergletscher (Fig. 1.6) with the legendary Dave Collins and his Manchester group. We sampled waters at hourly intervals during several days and nights, filtering the waters shortly after collecting them, and made pH measurements on the samples as quickly as we could. We measured cation concentrations on return to UEA by AAS (atomic absorption spectroscopy), and a big innovation was measuring the common strong acid anions, Cl^-, NO_3^- and SO_4^{2-}, by ion chromatography on another love of my life, the Dionex. This technology had been extended to more dilute solutions, partially as a result of the need to measure these species in acid rain. The SO_4^{2-} concentrations were at or almost zero in waters at maximum discharge, and I had stumbled on a way to distinguish between the two types of water which were then thought to be traveling through glaciers (more on this later). I became totally hooked on glacier meltwater hydrochemistry.

Figure 1.6 Switzerland's Gornergletscher, where Martyn got addicted to very dilute water.

We followed up with a second season at Glacier des Bossons in 1980, with my future best man, Paul Garrad, and Alan Thomas, Rob's first Ph.D. student. They both were fantastic in the field, totally unflappable whatever the weather and despite the odd working hours we had to keep. The closest they came to revolt was when I served up a sardine curry made from leftovers one evening. We repeated our work from Gornergletscher, finding broadly similar results. Sulphate seemed to be a key ion – it was concentrated in the concentrated waters, but virtually absent in the dilute waters. Writing up the work for my Ph.D. thesis revealed a few problems with using the common electrical conductivity-based mixing model that separated the runoff at the glacier terminus into two components of discharge, one that flowed rapidly from the glacier surface to the terminus and one that flowed slowly across the glacier bed. The composition of these two components could not be as constant as the literature of the time required. Rob continually nursed and kicked me through to getting my Ph.D., which was to be the last of the hand-written and hand-typed at Environmental Sciences, UEA.

I had the great honour of becoming an unemployed post-graduate in 1982, during the Thatcher cutback years. I worked first as a temporary chemistry school teacher, next as a well logger in the oil industry, and then I was incredibly fortunate to get a post-doctoral position back at UEA with Trevor Davies, Peter Brimblecombe and Chris Vincent, examining acid snow in Scotland. They were a great set of PIs to work for. The science was a hot topic. I was exposed

to a set of science politics and competition that was tough, but very stimulating. I learnt quickly that you had to publish or perish. Trevor and Rob were great influences on me. They were generous with ideas, contacts and polishing my tortured writing. They instilled an attitude that collaboration and cooperative effort usually wins in the long run, a philosophy that I've tried to maintain ever since, despite the burns every academic feels at times. I've tried to be like them since with my own graduate students and post-docs, but come up very short, of course.

1.6 Southampton – Where Oceanography and Glaciology Collided (MT)

The University sector contracted during the Thatcher cut-back years, and yet I was very fortunate to obtain a lectureship in Marine Sedimentary Geochemistry at Oceanography, Southampton, largely on the back of Rob's international reputation and the hope that some of his expertise must have rubbed off on me. I fell under the mentorship of Dennis Burton, another inspirational geochemist, and was hugely influenced by my friend, Peter Statham, on the need for good methodology in chemical analysis. I became immersed in putting together a marine geochemistry course, establishing a marine research profile, far from my glacier and acid snow days, when, out of the blue, Angela Gurnell knocked on my door.

1.7 Our Paths Converge (MT)

Angela and Mike Clark ran the GeoData Institute at Southampton, and were putting together a project on glacier hydrology at Haut Glacier d'Arolla in the Swiss Alps. They invited me to join them as a water chemist. I just couldn't say no. They were both incredibly generous to me in terms of encouragement and opening doors to collaboration. They set up a meeting with their Cambridge project partners, and I was introduced to the eminent fluvial geomorphologist, Keith Richards, and the soon to be eminent glaciologist, Martin Sharp. He was sharp..... Martin and I were left alone to talk a little science. He had read my thesis and managed to stay awake mostly. He asked me to explain and elaborate on a few things, and then explained back to me what I really meant to say in a much more elegant way. We hit it off immediately – we had the same interests, but very different backgrounds and methodologies to work away from. We both felt that the two component mixing model of glacier runoff was fine as a descriptive tool, but did not capture very well what we knew about hydrological and geochemical processes within and beneath small valley glaciers. We were determined to come up with something better, and the first phase of the Arolla project was about to deliver our wishes. Martin was one of the principal authors of the first Arolla grant applications, so I'll

let him set the scene for the project in terms of how glacier hydrology was viewed in the 1960's and 1970's.

2. GLACIER HYDROLOGY IN THE 1960's AND 1970's

2.1 Early Perspectives on Glacier Hydrology and Glacier Flow (MS)

Early thinking about glacier hydrology attempted to understand the mechanisms by which glacier flow and sliding occurred. It had been long known, since the work of J.D. Forbes (Fig. 2.1) on the Mer de Glace (Chamonix) in the 1840's, that the velocity of a glacier can vary seasonally, being higher in summer, when meltwater is abundant, and lower in winter, when meltwater is either absent or much less abundant. By the 1960's, it was also known that meltwater efflux from glacier termini varied seasonally and diurnally (in summer), more or less in parallel with variations in surface melt rates.

Figure 2.1 James David Forbes.

Early efforts at drilling and tunnelling through glaciers (*e.g.,* Mathews, 1964) had encountered englacial water pockets, so it was clear that there had to be a meltwater drainage system within glaciers that connected the surface to the terminus. Observations in a shaft beneath Canada's South Leduc Glacier had found variations in water pressure at the bed that were connected to the occurrence of rainfall and melt events on the glacier surface (Mathews 1964). From the 1940's, a number of workers made measurements of the rate of movement of glacier soles in natural cavities and tunnels, finding that there was measurable displacement between the glacier and its bed (Carol, 1947; Haefeli, 1951; Kamb and LaChapelle, 1964). Velocities measured at glacier beds were often spatially variable and always less than velocities measured nearby at the glacier surface. Surface velocities clearly varied over time and measurements of water pressure at the bed suggested that this might be connected to hydrologically-forced fluctuations in basal friction. From these observations, it was clear that

there must be at least 2 processes of glacier flow – one involving the deformation of the ice itself, and another involving displacement of the ice relative to the bed (or sliding), which might be affected by variations in the flux and pressure of subglacial water.

2.2 The Development of Theory Relating Glacier Hydrology and Glacier Flow (MS)

The first quantitative theory of glacier sliding (Weertman, 1957) argued that sliding occurred when the ice at the bed was at the pressure melting temperature, and that it arose from the sum of two processes – regelation and enhanced viscous deformation. These are both linked to the fluctuations in ice-bed contact pressure that occur as a glacier moves past roughness elements (or bumps) on its bed.

Because the ice is at the pressure melting temperature, and the pressure is higher on the upstream side of the bump than on the downstream side, so the ice temperature on the upstream side is lower than it is on the downstream side, where pressure is lower. The resulting temperature gradient across the bump means that heat flows through the rock from the downstream side to the upstream side, causing melting on the upstream side. The water produced by this melting flows along the gradient from high to low pressure that exists across the bump. As this water is colder than the ice on the downstream side, it refreezes when it gets to the lee side of the bump. The latent heat of refreezing that is released flows back through the bump to drive melting on the upstream side. This process only works for relatively short wavelength bumps, but it creates short length-scale (from several cm to several m) meltwater drainage systems at the glacier bed, associated with topographic irregularities.

Where the bedrock is highly soluble in water (as is limestone, for instance), the meltwater in the regelation water film may dissolve the bedrock on the upstream side of a bump, transport the resulting solute around the bump to the leeside, and then precipitate it in mineral form on the leeside, where refreezing rejects solute and concentrates it to the point of supersaturation (Fig. 2.2). Since the presence of solute in the water alters the temperature at which the water will freeze, there is a feedback on both the regelation process and the flow of the glacier. Geomorphological evidence from recently deglaciated limestone surfaces supports this idea very clearly (Hallet, 1976a; Walder and Hallet, 1979; Hallet and Anderson, 1980). This is perhaps the first work to articulate clearly a coupling between subglacial hydrology, glacier flow, and subglacial geochemical processes.

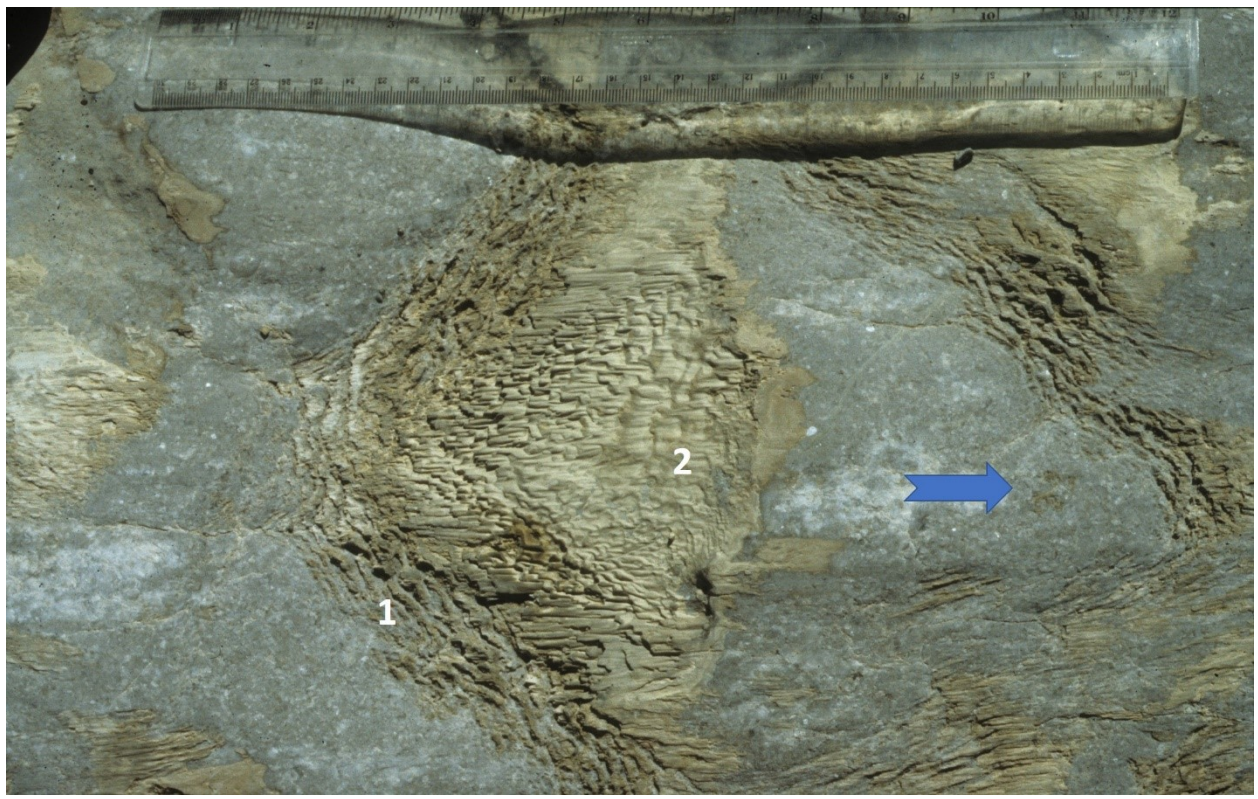

Figure 2.2 Formerly glaciated limestone bedrock surface at the Glacier de Tsanfleuron, Switzerland, showing dissolution furrowing (1) on the upstream side of a bedrock bump where pressure-induced melting would have occurred, and subglacial calcite precipitation (2) on the downstream side where low pressures, refreezing and solute concentration would have occurred. Glacier flow was from left to right (modified from Sharp *et al*.,1989).

2.3 Glacier hydrochemistry in the 1970's (MT)

The Earth Science community tended to think that much of the glacier bed was frozen to bedrock, and that the lack of water and low temperatures precluded very much chemical weathering (Gibbs and Kump, 1994). Glaciers were also thought to be biologically inert, since earth scientists and glaciologists found it very difficult to believe that microbes could function in the cold and dark (Raiswell and Thomas, 1984). Glacial meltwaters that were sampled were often quite dilute (Raiswell, 1984) and, as such, they offered little of interest to geochemists at the time. However, there were a few things to interest anyone interested in dissolving sparingly soluble silicate minerals.

Glaciers are powerful agents of physical erosion, pulverising or comminuting the bedrock they flow over, producing glacial flour. Early work on glacier meltwater geochemistry aimed to show that glacial flour produced fertile soils, because of the relative ease with which cations could be obtained by plants from the flour. Glacial meltwaters easily transport the flour and are milky

as a consequence (Keller and Reesman, 1963), often containing ~1 g L^{-1} of fine suspended sediment. The grains are often mainly silt- to clay-sized (Keller and Reesman, 1963; Hallet *et al*., 1996), and this maximises the potential for minerals to dissolve. The meltwater chemistry of runoff from a variety of glaciers in the USA, the Alps, Norway and Antarctica could be simulated in the laboratory by grinding rocks in double distilled water. Hydrolysis, the interaction of water with the surfaces of silicate minerals such as feldspars, was thought to generate the solute (equation 2.1),

$$NaAlSi_3O_8\ (s) + H_2O\ (l) \leftrightarrow HAlSi_3O_8\ (s) + Na^+\ (aq) + OH^-\ (aq) \quad (2.1)$$

where $NaAlSi_3O_8$ is a sodium-bearing feldspar, such as albite, and $HAlSi_3O_8$ is a partially weathered or leached feldspar surface. The pH of the solution becomes quite high (up to 9.8), because of the hydroxide ions (OH^-) produced. Mafic rocks, those containing a preponderance of ferro-magnesian minerals, gave rise to more solute than felsic rocks, those containing a preponderance of feldspar and quartz. However, carbonates yielded the most solute, because carbonate hydrolysis completely dissolves the surface of the mineral, rather than leaving behind a leached surface layer.

$$CaCO_3\ (s) + H_2O\ (l) \leftrightarrow Ca^{2+}\ (aq) + HCO_3^-\ (aq) + OH^-\ (aq) \quad (2.2)$$

A strange feature of the lab simulations was that the pH of the ground rock slurries was usually 1-4 pH units higher than that of the glacial milks they were attempting to simulate. This was presumed to be due to the ingress of more atmospheric CO_2 into natural solutions. This was an important observation, which we expand on further below. This early work was followed by studies of meltwater streams draining Alaskan glaciers, which showed that the overall concentrations of solutes in the streams were not correlated with the bedrock type (Fig. 2.3 and Table 2.1 (Slatt, 1972)). The meltwaters gained solute during storage if they were not filtered immediately following collection. Hence, interactions between the suspended sediment and the meltwater after sampling could result in solute acquisition by the water.

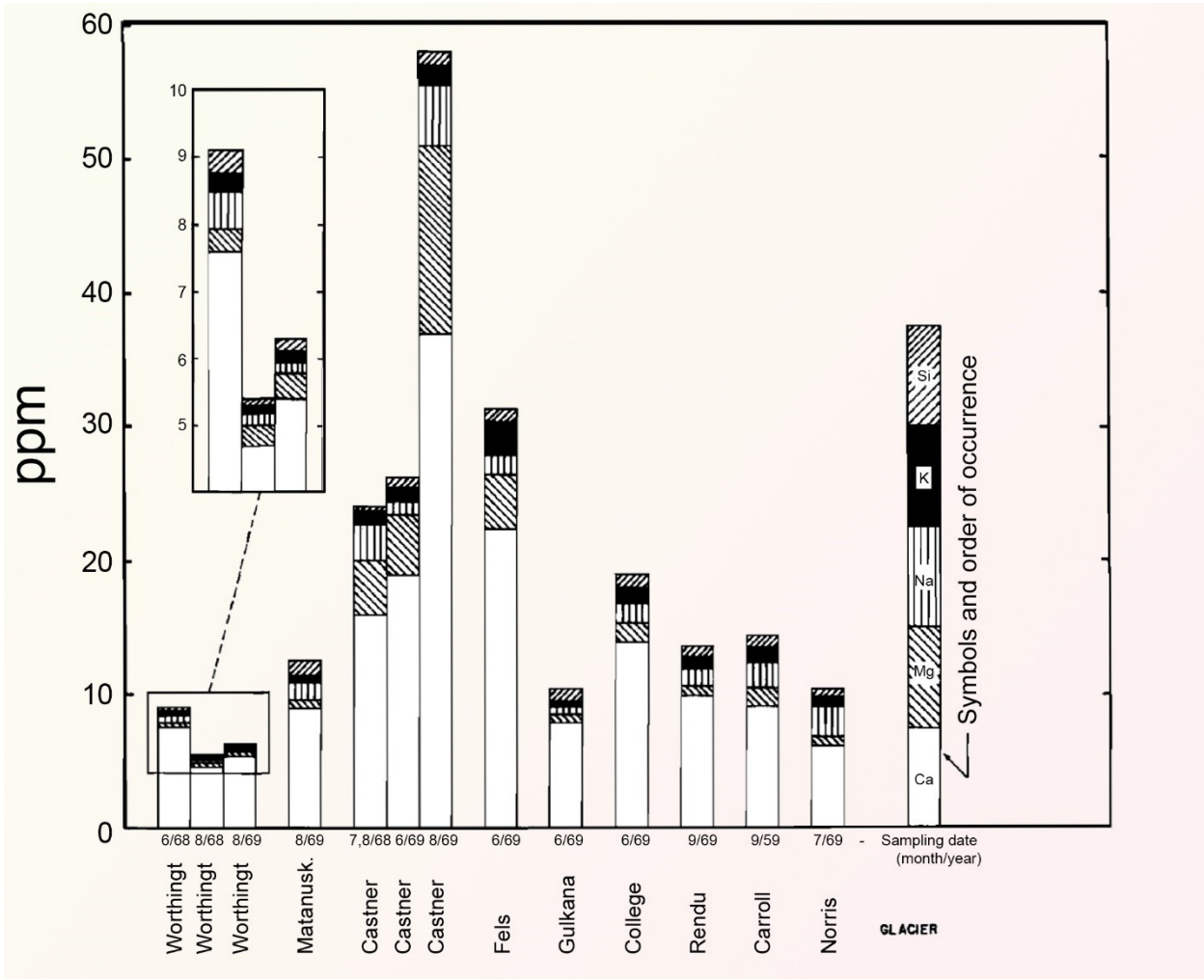

Figure 2.3 Major cation and dissolved Si concentrations in meltwaters from 9 Alaskan glaciers (modified from Slatt,1972). Figures in those days were drawn by hand, and labelling was not always as bold as brass. The Y axis is the concentration in units of ppm. The first three samples on the left come from Worthington Glacier (sampled in 1968 and 1969), the next is from Matanuska Glacier (1969), followed by three from Castner Glacier (1968 and 1969), followed by one each from Fels, Gulkana, College, Rendu, Carroll and Norris Glaciers (1969). Note that Ca^{2+} is always the dominant cation in all samples analysed (lowest white space on column), usually folled by Mg^{2+} (diagonal stripes sloping down from the left), and that Na^{+} (vertical lines), K^{+} (black) and Si (diagonal stripes sloping up from the left) are present in relatively low concentrations.

Table 2.1 Location and bedrock geology of Alaskan glaciers sampled for analyses of water chemistry (modified from Slatt, 1972).

TABLE 1. LOCATION AND BEDROCK TERRANE OF GLACIERS

Glacier	N. Lat	W. Long	Locale	Dominant bedrock type(s)
Worthington	61°10'	145°45'	Chugach Mtns.	Phyllitic graywacke[1]
Matanuska	61°20'	148°40'	Chugach Mtns.	Phyllitic graywacke[2,3]
Castner	63°25'	145°40'	Alaska Range	Quartz-mica schist[4]
Fels	63°23'	145°38'	Alaska Range	Quartz-mica schist[4]
Gulkana	63°18'	145°25'	Alaska Range	Complex igneous, sedimentary and metamorphic rocks[5]
College	63°15'	145°21'	Alaska Range	Complex igneous, sedimentary and metamorphic rocks[5]
Rendu	59°04'	136°50'	Alaska Coast Range	Granodiorite and metasediments[6,7]
Carroll	59°01'	136°30'	Alaska Coast Range	Dioritic gneiss[7]
Norris	58°24'	134°08'	Alaska Coast Range	Quartz dioritic to granodioritic gneiss[8]

[1] *Coulter and Coulter (1961)*
[2] *Dutro and Payne (1954)*
[3] *Grantz (1961)*
[4] *Moffitt (1954)*
[5] *Bond (1965)*
[6] *Rossman (1963)*
[7] *MacKevett and others (1967)*
[8] *Forbes (1959)*

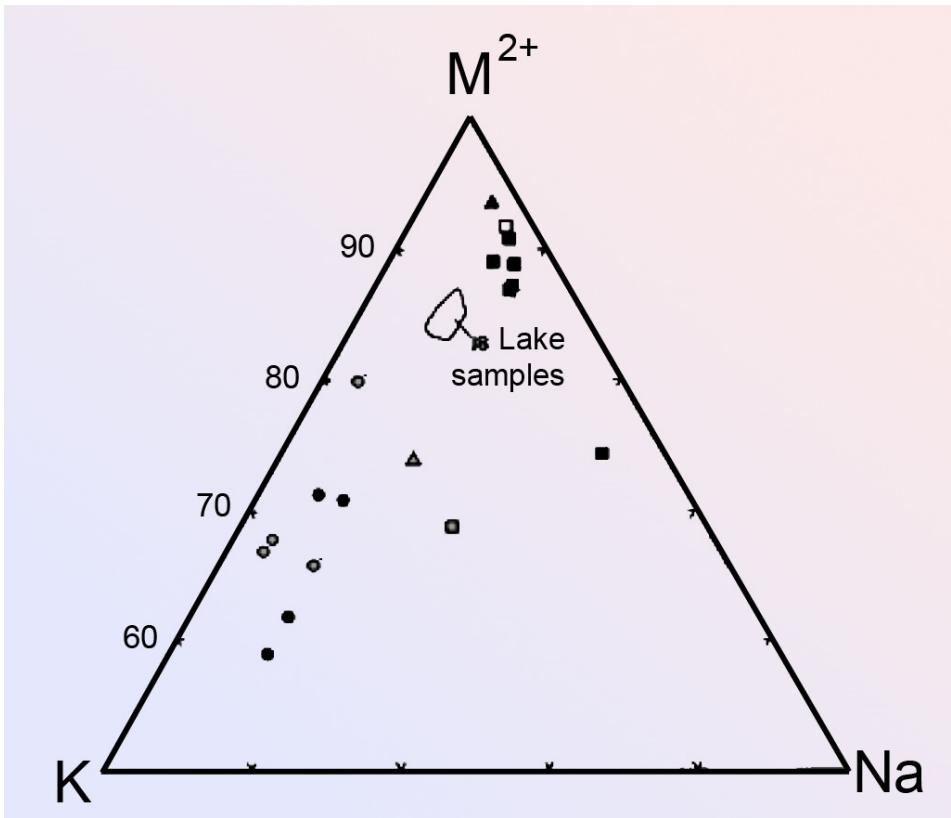

Figure 2.4 Major cation chemistry of meltwaters from the vicinity of South Cascade Glacier, Washington State USA, in relation to bedrock geology (M^{+2} means Ca^{2+} + Mg^{2+}) (modified from Reynolds and Johnson, 1972).

Meanwhile, seminal work was being conducted in the catchment of the South Cascade Glacier in the North Cascades Mountains of Washington State, USA (Fig. 2.4; Reynolds and Johnson

1972). Samples were collected over an ablation season, and efforts were made to measure both SO_4^{2-} and HCO_3^- , so that chemical weathering mechanisms could be determined. The positive association between the major base cations and HCO_3^- suggested that carbonation was occurring. Carbonation of silicates and carbonates (equations 2.3 and 2.4) occurs when dissolved CO_2 (which forms carbonic acid, H_2CO_3) interacts with mineral surfaces, in a reaction that is otherwise similar to hydrolysis (equations 2.1 and 2.2). The pH does not increase so much as in hydrolysis because OH^- is not a primary reaction product.

$$NaAlSi_3O_8\ (s) + H_2O\ (l) + CO_2\ (aq) \leftrightarrow HAlSi_3O_8\ (s) + Na^+\ (aq) + HCO_3^-\ (aq) \quad (2.3)$$

$$CaCO_3\ (s) + H_2O\ (l) + CO_2\ (aq) \leftrightarrow Ca^{2+}\ (aq) + 2HCO_3^-\ (aq) \quad (2.4)$$

There was also a good correlation between HCO_3^- and SO_4^{2-}. The SO_4^{2-} was thought to be derived from sulphide oxidation (equation 3.5). Sulphide minerals, such as pyrite (FeS_2), are ubiquitous components of many types of bedrock (Reynolds and Johnson, 1972). Hence, sulphide oxidation was occurring in the catchment and was a principal geochemical weathering reaction. However, the cause of the association between these ions was otherwise unclear. A big conclusion of the work was that the cation flux from the South Cascade Glacier catchment was almost 3 times the average flux from other temperate river basins in North America, despite the meltwaters being cold and dilute. This was attributed to the constant flushing of finely crushed glacial debris by meltwater, which maximised the dissolution rate (Reynolds and Johnson, 1972). The magnitude of this flux was contrary to expectations, and suggested that chemical weathering in glaciated catchments merited further attention.

It was believed by some that surface exchange added cations to solution (Lemmens and Roger, 1978), although the mechanism of surface exchange was poorly defined. Surface exchange is now probably best thought of as the rapid initial hydrolysis reaction between crushed silicates and water (Keller and Reesman, 1963). Some felt that there was potential for more cations to be liberated from the surface of the glacial flour, since sorption was seen as a means of transporting cations (Lorrain and Souchez, 1972). A key result in the field was the observation that the solute content of Alpine glacial meltwaters was not correlated with suspended sediment concentration (Collins, 1979a), which implied that the meltwaters were acquiring solute in environments other than the channels carrying the bulk of the turbid water. What was certain was that more chemical weathering was occurring in glacial environments than in nearby un-glaciated regions (Church, 1974), that Ca^{2+} was the most common cation, irrespective of bedrock type (Raiswell, 1984), and that Mg^{2+} was usually the second most

common. Na^+ and K^+ were only relatively common on andesitic and granitic bedrocks (Keller and Reesman, 1963; Raiswell, 1984), after correcting for sea salt effects.

Finally, only the common base cations had been measured routinely (Raiswell, 1984). Alkalinity, essentially HCO_3^-, was seldom reported. Some corresponding pH measurements were made, but these were tricky to perform accurately because of the low solute concentrations present and the high suspended sediment concentrations (Bates, 1973). This meant that it was difficult both to determine the mechanisms of chemical weathering and the factors which drove the chemical weathering after the initial phase of surface exchange/hydrolysis. This brief summary of the literature of the time suggested to me that the mechanisms of rock-water reactions in glacial meltwaters were not really well-established, and neither was the locus of the geochemical weathering. Crushed rock, dilute solutions, and the search for rock-water interactions was the combination that caught my imagination. The small literature base that I could get my head around and still play a lot of cricket helped enormously too.

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3. GLACIER HYDROLOGY AND HYDROCHEMISTRY IN THE 1980's: TWO COMPONENT MIXING MODELS (MT)

One of the most striking features of runoff from Alpine glaciers in the summer is the large diurnal variation in discharge during the period after the snow cover on the lower glacier has been ablated (Fig. 3.1). Variations in discharge are inverse to those of electrical conductivity (EC) on a diurnal basis (Fig. 3.2), and over the ablation season as a whole (Fig.3.3), although there is much scatter in the data. EC increases as the concentration of total solutes increases, although supplementary chemical measurements are required to determine the absolute composition of the solute.

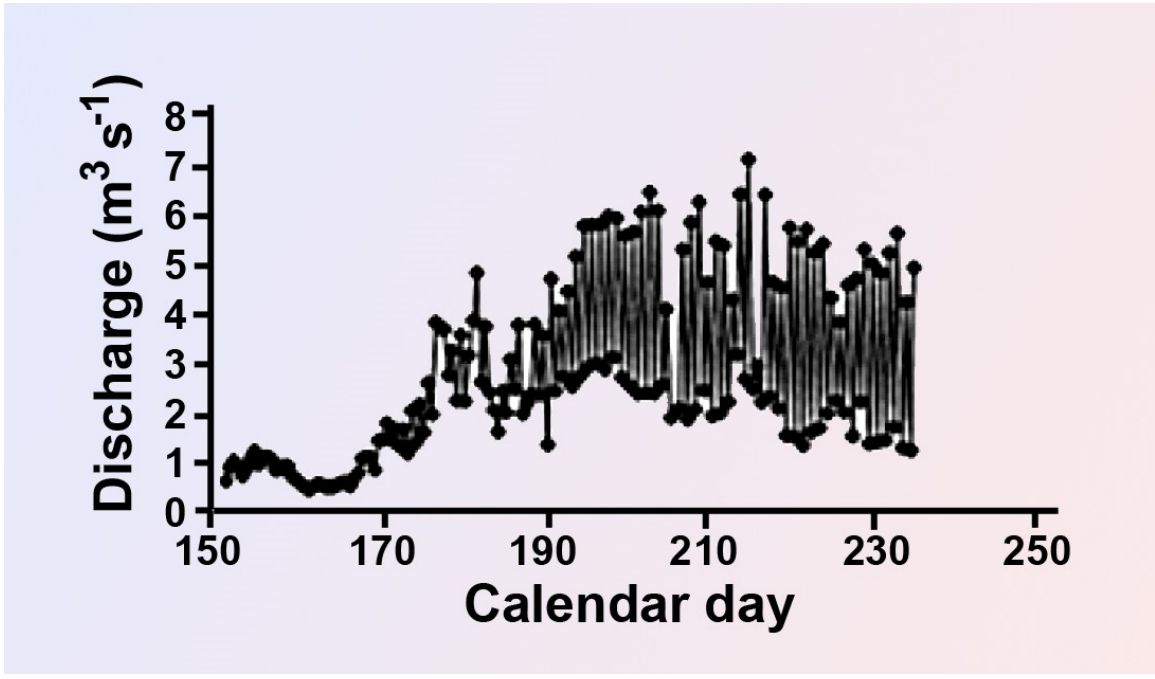

Figure 3.1 Variations in bulk meltwater discharge from Haut Glacier d'Arolla, Switzerland, from June 1 (day 152) to August 31 (day 243), 1990 (modified from Brown, 2002).

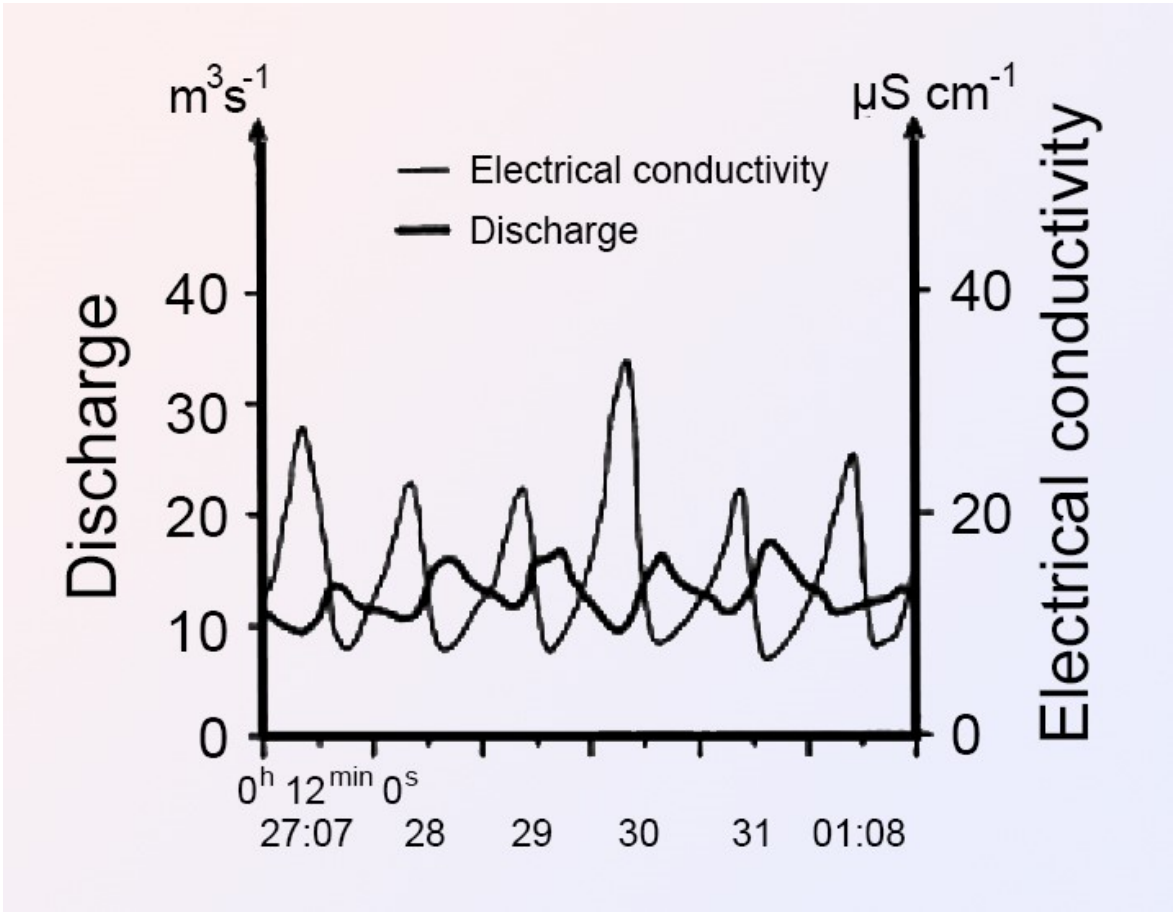

Figure 3.2 Temporal variations in the electrical conductivity of meltwater runoff and discharge from the Gornergletscher, Switzerland, from July 27 to August 1, 1975 (modified from Collins, 1979a).

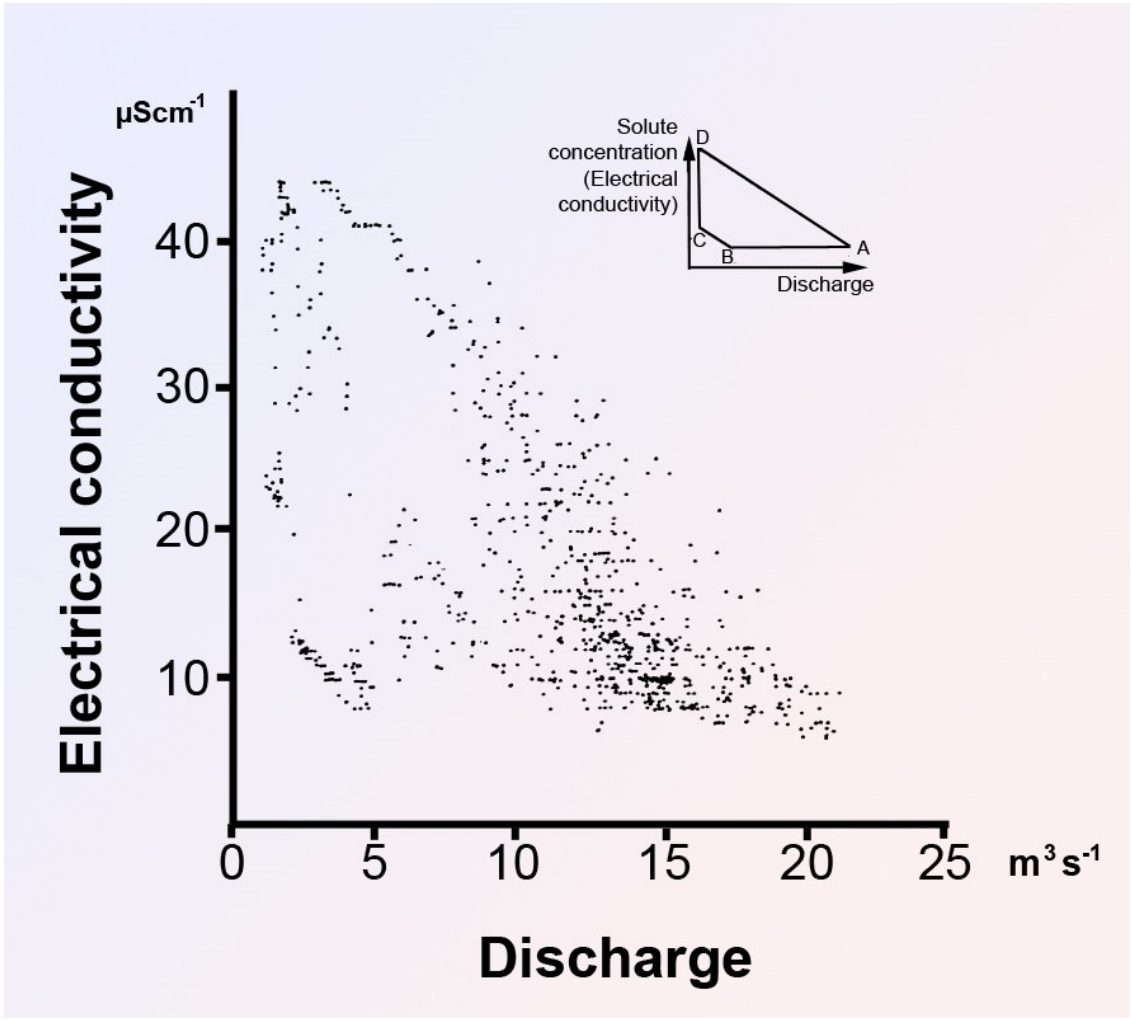

Figure 3.3 Relationship between the electrical conductivity of meltwaters draining from the Gornergletscher and meltwater discharge during the summers of 1974 and 1975 (modified from Collins, 1979a).

David Collins, then at Geography, University of Manchester, pioneered the simultaneous measurement of discharge and electrical conductivity variations in glacier-fed streams, and started the debate about what the measured variations actually show. He worked principally at Gornergletscher and Findelengletscher in the Swiss Alps. David argued that a concentrated component of subglacial runoff was variably (and seasonally) diluted by surface (or *supraglacial*) snow and ice melt, producing low conductivity runoff at high discharges. He assumed that the two flow components mixed conservatively, both in terms of the amount of water and the total amount of solutes, and produced a number of compelling hydrograph separations (Fig. 3.4).

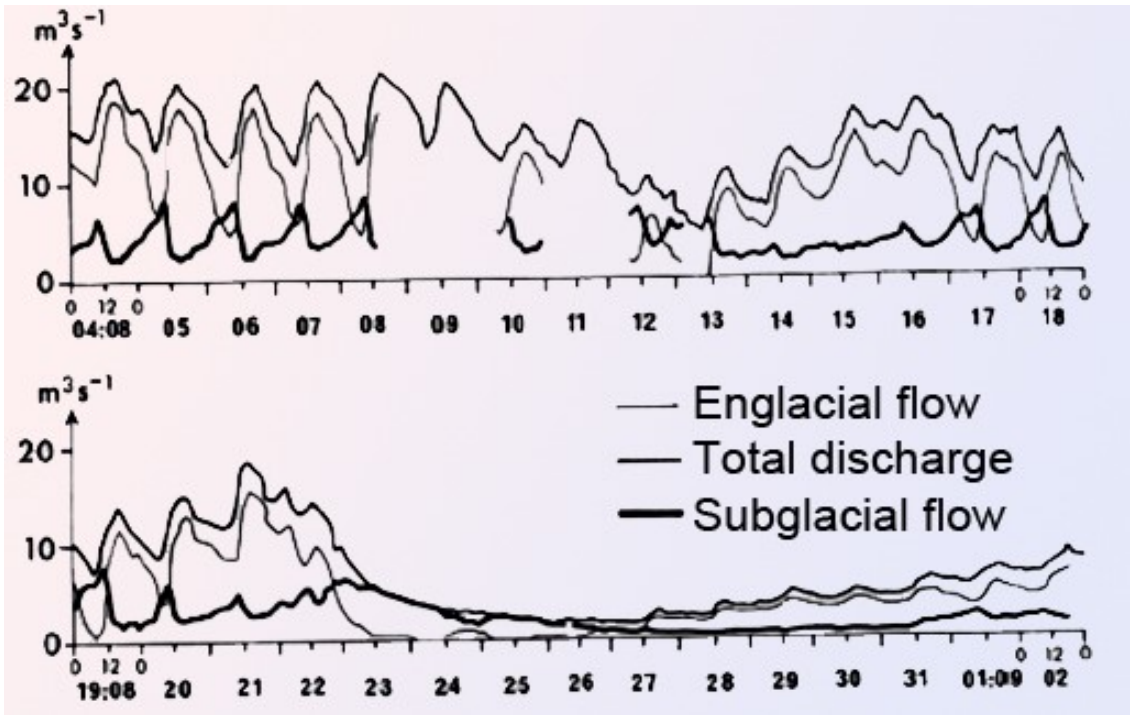

Figure 3.4 Separation of the bulk runoff from Findelengletscher into two components, englacial and subglacial flow (see Text Box 3.1) (modified from Collins, 1979b).

Text Box 3.1 – Equations that describe the two component mixing model (2CCMM)

The two component conservative mixing model (2CCMM) requires that the discharge of glacial runoff (Qb) is made up of two components, the englacial component, with water flux Qe, and the subglacial component, with water flux Qs. Hence,

$$Qb = Qe + Qs \qquad (3.1)$$

The solute flux in the glacial runoff, QbCb, where Cb is the concentration of a chemical species of interest in the bulk runoff, comes from the sum of the englacial flux, QeCe, and the subglacial flux, QsCs, where Ce and Cs are the concentrations of the species of interest in the englacial and subglacial components respectively. It follows that

$$Qb\ Cb = Qe\ Ce + Qs\ Cs \qquad (3.2)$$

A time series of Qb, a hydrograph, can be separated into time series of englacial and subglacial water fluxes, Qe and Qs, by combining equations (3.1) and (3.2) such that

$$Qe = Qb\ (Cs-Cb)/(Cs-Ce) \qquad (3.3)$$

and

$$Qs = Qb\ (Cb-Ce)/(Cs-Ce) \qquad (3.4)$$

EC has often been used as a proxy for the total concentration of solutes in meltwaters. It should be noted, however, that the same concentrations of different solutes give rise to different EC values. Usually, this is not a big problem if the pH is in the range of ~4.5 to ~9.5, since H^+ and OH^- have a disproportionate influence on EC in comparison to other ions.

This two component conservative mixing model (2CCMM) is constructed from two equations with six variables (see Text Box 3.1), only two of which are measured and known - the discharge and conductivity of the glacial runoff. It follows that two of the four unknowns had to be somehow estimated in order to solve for the other two unknowns. Collins estimated the EC of the dilute supraglacial water, known as the *englacial component*, and the concentrated *subglacial component* as the lowest and highest conductivities measured in the bulk runoff over the course of the ablation season, and assumed that these values were constant throughout the melt season. This was a step jump forward for the discipline at the time, and resulted in a great deal of debate about the nature of water flow paths both through and beneath small, warm-based valley glaciers.

3.1 Hydrologically-Based Challenges to the Two Component Conservative Mixing Model (MS)

Unfortunately, the model was almost immediately challenged by work on snowmelt chemistry, the results of careful geomorphological studies of recently deglaciated glacier beds, and emerging theoretical models of subglacial drainage. The scientific debate about the causes of acid precipitation and runoff in the 1970's promoted a number of detailed studies of the chemistry of snowmelt runoff. An early finding of this work was that solute was preferentially eluted from snowpacks during the initial stages of melt (Johannessen and Henriksen, 1978). One consequence of this is that snowmelt chemistry is not constant over time. Another is that, in regions where snow is converted to glacier ice in the presence of surface melting and refreezing, the resulting glacier ice is often solute depleted relative to the original snowpack (Sharp *et al*., 1995a). This implies that there is no unique and constant solute concentration in glacial meltwaters produced by surface melting of snow and ice, and that the chemistry of surface runoff likely changes over time, becoming more dilute as the seasonal snowpack is flushed of solute and removed, and as glacier ice is exposed and becomes a more significant

source of runoff. This realisation undermined one of the fundamental assumptions of the 2 component mixing model, that meltwaters entering the glacier surface had a temporally uniform chemical composition.

At the same time, studies of the morphology of glacier beds, particularly in carbonate terrains (Walder and Hallet, 1979; Hallet and Anderson, 1980) strongly suggested that subglacial drainage systems had multiple components that were likely associated with different rates of flow transmission. These components likely produced waters with quite different mean chemical compositions, and chemical compositions that varied over time as discharge and subglacial residence time changed. These system components included:

(i) a ***subglacial water film*** associated with the regelation process (Weertman, 1957).

(ii) ***cavity systems*** (Fig. 3.5) formed by ice-bed separation downstream of bedrock bumps that were connected together by networks of small channels dissolved/eroded into the bedrock (Lliboutry, 1968; Walder, 1986; Kamb, 1987).

(iii) ***large channels*** incised up into the ice (R-channels) that were likely fed by supraglacial meltwater that was able to reach the glacier bed (Röthlisberger, 1972). Sedimentary landforms known as "eskers" thought to be deposited in such channels are widespread on some sections of the beds of former Quaternary ice sheets in Europe and North America (Sugden and John, 1976).

(iv) deep ***rock-walled channels*** incised into the glacier bed, known as N-channels (Nye, 1976), which are also very visible in many deglaciated terrains (Sugden and John, 1976).

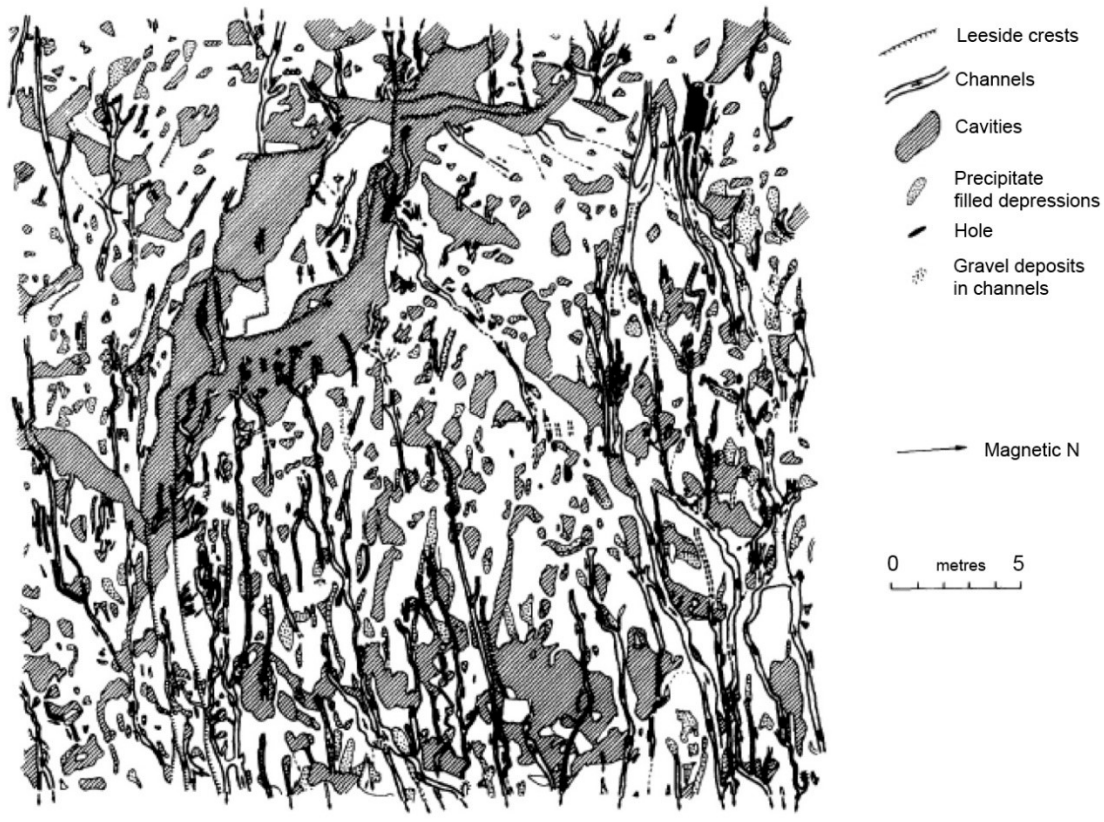

Figure 3.5 Detailed geomorphological map of an area of the recently deglaciated bed of Glacier de Tsanfleuron, Switzerland, showing the distribution of formerly water-filled leeside cavities, Nye channels incised into bedrock, and depressions filled with calcite precipitates (from Sharp *et al.*,1989).

Given this heterogeneity of potential drainage pathways, it was clear that the *ad hoc* and convenient assumption that glacier drainage systems had just 2 distinct components (englacial and subglacial) was untenable. Subsequent work (by Garry Clarke, Joe Walder, and Andrew Fowler) on the physical hydrology of active glacier beds underlain by layers of sediment, often with multiple permeabilities and spatially and temporally varying thicknesses, added additional complexity (Clarke *et al.*, 1984; Fowler and Walder, 1993; Walder and Fowler, 1994). Glacier drainage systems appeared to be structurally and functionally more complex than the 2 component mixing model allowed. Their extent and structure appeared to be capable of changing over time (on a range of different timescales) and for reasons that involved interactions between runoff volume, channel geometry, drainage network structure and tortuosity, glacier-bed separation, bed stability (especially for sedimentary beds), and glacier dynamics. It seemed implausible that systems with such complexity, when subjected to temporally and spatially varying meltwater inputs, could yield just two distinct runoff

chemistries and that those chemistries could conceivably be time-invariant as was assumed by the formulation of the two component chemical mixing model (Sharp *et al.*,1995a).

The time had clearly come to start investigating the time-varying behaviour of subglacial drainage systems directly. Such work was accelerated, in part at least, by interest in explaining how fluctuations in meltwater runoff might affect rates of glacier flow (Iken, 1981; Iken and Truffer, 1997), and the need to understand such phenomena as fast glacier flow in ice streams (Engelhardt *et al.*, 1990) and glacier surging (Kamb *et al.*,1985; Kamb, 1987), which were the focus of an AGU Chapman Conference in 1987. A growing number of scientists thought that these phenomena might have an explanation in the interactions between meltwater flux, drainage system structure, and glacier flow.

3.2 Chemically-Based Challenges to the Two Component Conservative Mixing Model (MT)

Water chemists also had several problems with the 2CCMM, revolving around why the composition of the "subglacial" component would be constant throughout the ablation season. Waters become more concentrated when the duration of contact (the rock-water contact time) increases, and/or when the amount of rock *per* unit of water (the rock-water ratio) increases. Both these variables must change both temporally as the ablation season progresses, and spatially, given the heterogeneous nature of glacier beds. A more philosophical point is that most dynamic environmental chemical systems are controlled by reaction kinetics. It is rare for waters to attain relatively constant compositions because equilibrium conditions have been reached. Rather, the compositions are controlled by how fast the minerals dissolve relative to the speed at which the water travels across the rock. Just how the components could have fixed, constant compositions when parameters such as the length of the flow path, water velocity, residence time in the subglacial drainage system, suspended sediment concentration, sediment mineralogy, and access to atmospheric gases would all be changing over the ablation season was hard to understand. We felt that although the 2CCMM had been a useful descriptive tool, it did not stand up to scrutiny as a representation of how meltwater drained across glacier beds and acquired solute in the process. Its use to interpret drainage system behaviour therefore likely concealed more than it revealed.

3.3 New Perspectives on Meltwater Chemistry (MT)

Rob Raiswell and Alun Thomas at UEA were changing the way researchers viewed glacial meltwater geochemistry (Raiswell, 1984; Raiswell and Thomas, 1984; Thomas and Raiswell,

1984). We noted above that the glacial literature focused for a while on ion exchange as a means of adding solute to solution. Rob was always sceptical that ion exchange added solute to solution *per se* – exchanging the surface cations on the crushed minerals for ions already in solution resulted in no net addition of solute to solution. We both felt that the devil in the detail of surface exchange held the key to what drove chemical weathering in turbid meltwaters, and this is what we came up with.

Hydrogen ions (H^+) from solution exchanged for the cations on mineral surfaces, forcing up the pH, increasing the solubility of dissolved CO_2 species in solution, and drawing CO_2 into solution from the atmosphere (see Text Box 3.2). The hydrogen ions came from CO_2 interacting with water to form carbonic acid, H_2CO_3 and the carbonic acid dissociating into H^+ and HCO_3^- ions (equation 3.8). Rob and Alun had found that some meltwaters were saturated with atmospheric CO_2 – so-called open systems (Thomas and Raiswell, 1984), while others were undersaturated – so-called closed systems (Raiswell and Thomas, 1984). They thought that if atmospheric CO_2 could access the glacier bed, then the weathering systems would be open, whereas if it could not, then they would be closed. My gut feeling was that the character of the glacier drainage system was not the only factor involved here. It occurred to me that open weathering systems could also be those in which the water-rock reactions took place at the same rate as that at which CO_2 could be supplied to the waters, whereas closed systems could be those in which water-rock reactions consumed CO_2 faster than the rate at which the CO_2 supply could be replenished. This seemed a terribly nerdy and pedantic point of view, but it provoked a step change in the way I thought about chemical weathering under glaciers – the crushed rock could react more if you could only give it enough H^+, and where the acid came from was the key to whether or not this was possible.

The first of the two principal sources of H^+ to most earth surface chemical weathering environments is CO_2 dissolving in water to form carbonic acid, and this weak acid dissociating to form an HCO_3^- anion and an H^+ ion (equation 3.8). At the time, we assumed that the main source of CO_2 was the atmosphere. The second important reaction was the oxidation of sulphide to produce sulphuric acid (equation 3.5), a process which is the origin of highly acidic mine drainage waters.

$$4FeS_2\,(s) + 14H_2O\,(l) + 15O_2\,(aq) \leftrightarrow 4Fe(OH)_3\,(s) + 8H_2SO_4\,(aq) \quad (3.5)$$

Sulphides are ubiquitous in most types of rock, and glacial erosion of bedrock liberates sulphides from their enveloping rock, making them available for reaction. Crushing of rocks also removes and limits the build-up of oxide and organic coatings on the mineral surfaces,

making them more available for reactions with water. The same is true for carbonate minerals – they are pervasive in most types of rock and are also liberated for reaction by glacial erosion. Every schoolchild knows that if you add sulphuric acid to chalk (a carbonate mineral), you dissolve the chalk and produce a fizzy solution that is over-pressured with CO_2. This solution has closed system characteristics, in that it is out of equilibrium with the atmosphere, and is referred to as high pCO_2 closed system. The surface exchange type of silicate weathering, described above, produces a low pCO_2 closed system in stark contrast. This type of solution doesn't fizz, but actively tries to suck CO_2 out of any atmosphere or bubbles of atmospheric gas it comes into contact with.

My first field season as a Ph.D. student was at Gornergletscher, and this allowed me to sample and filter meltwater samples quickly, to avoid reactions between the water and suspended sediment. I was also quick to measure pH in the best way we could at the time, so minimising drift effects. The advent of ion chromatography allowed me to measure low SO_4^{2-} concentrations in glacial meltwaters with confidence for the first time. These concentrations were undetectable at high discharges (Fig 3.6) and in the surface meltwater streams we sampled. Thus SO_4^{2-} was almost exclusively generated by chemical weathering reactions at the bed. We made some educated guesses, which time has shown were not so educated, and derived a means of estimating the SO_4^{2-} concentration of the subglacial component, and separated the Gornergletscher hydrograph on two different days (Fig 3.6), in which our estimated SO_4^{2-} concentrations in the subglacial component were different. The methodology has not stood the test of time, but the principle of using specific reactions to fingerprint flow components and not to assume invariant end member compositions over time remains.

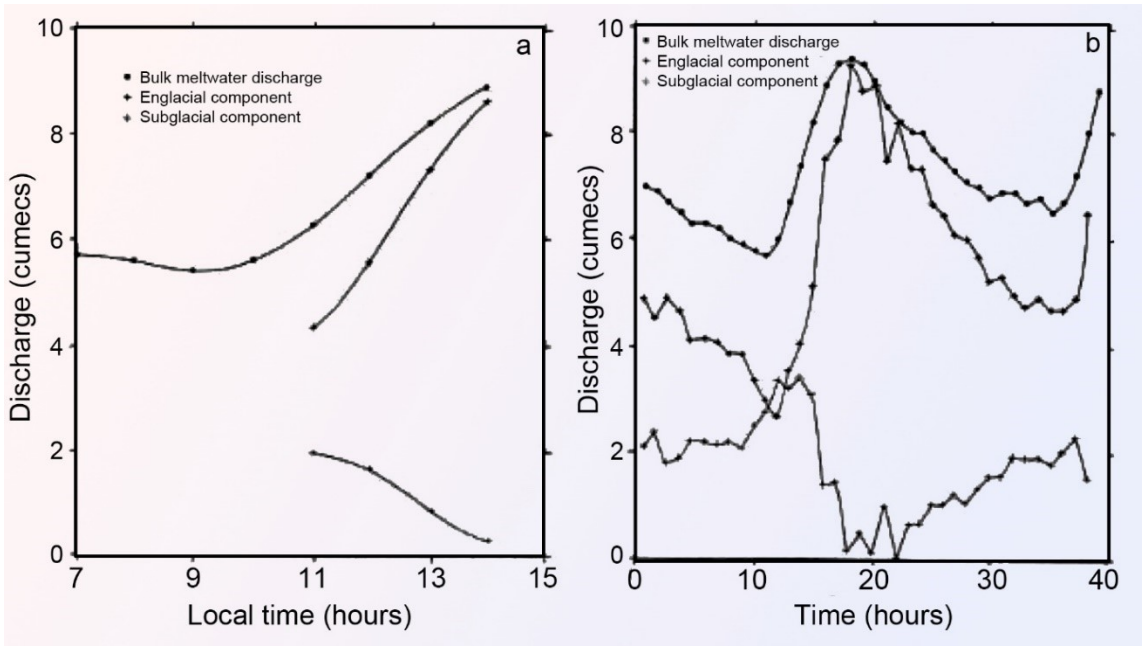

Figure 3.6 Variation in meltwater chemistry **(a)** 16 September (A samples); **(b)** 18-20 September (B samples). Note that sulphate concentrations for the B samples were estimated from the charge balance deficit (modified from Tranter and Raiswell, 1991).

I collected a pitiful amount of data for my Ph.D. thesis in comparison to what modern Ph.D. students would assume they need for a credible thesis. We needed “more data”, which was one of Rob’s constant reminders to a lazy Ph.D. student. A recurrent theme throughout my research career is that as soon as you think you’ve got something figured out, a curveball comes to complicate what you thought was simple. The first Arolla project was to throw up a few curveballs, and my first post-graduate student, Giles Brown, who was co-supervised by Angela Gurnell and Mike Clark, didn’t even know he was about to play baseball.

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Text Box 3.2

Gaseous (g) carbon dioxide (CO_2) will always try to equilibrate with CO_2 dissolved in water (aq), as shown in equation (3.6).

$$CO_2\ (g) \leftrightarrow CO_2\ (aq) \quad (3.6)$$

The dissolved CO_2 interacts with water to form carbonic acid (H_2CO_3), which dissociates to form an H^+ ion and a bicarbonate anion (HCO_3^-) as shown in equations (3.7) and (3.8).

$$CO_2\ (aq) + H_2O\ (l) \leftrightarrow H_2CO_3\ (aq) \quad (3.7)$$

$$H_2CO_3\ (aq) \leftrightarrow H^+\ (aq) + HCO_3^-\ (aq) \quad (3.8)$$

HCO_3^- can also dissociate into carbonate (CO_3^{2-}) ions, releasing another H^+ ion. This reaction becomes increasingly important at pH above ~9.3.

$$HCO_3^-\ (aq) \leftrightarrow H^+\ (aq) + CO_3^{2-}\ (aq) \quad (3.9)$$

The H^+ ion is important, since it is small and easily exchanges for a base cation (Ca^{2+}, Mg^{2+}, Na^+ and K^+) in the surface of crushed rock. This is the basis of many geochemical weathering reactions. Equation (3.9) gives an example of a sodium feldspar ($NaAlSi_3O_8$) being chemically weathered by H^+, giving rise to Na^+ in solution and a partially weathered feldspar surface ($HAlSi_3O_8$).

$$NaAlSi_3O_8\ (s) + H^+\ (aq) \leftrightarrow HAlSi_3O_8\ (s) + Na^+\ (aq) \quad (3.10)$$

LeChatelier's Principle states that if you remove a species from one side of a chemical equation, more of the reactants on the other side of the equation will interact to make good the removal of the species. Equation (3.10) effectively removes H^+ from the right hand side (RHS) of equation (3.8), which in turn uses up carbonic acid from the left hand side (LHS) of equation (3.8) to make good the deficit. This in turn uses up CO_2 (aq) from the LHS of equation (3.7) to make up that deficit, which in turn forces more CO_2 into solution to make good the loss of CO_2 (aq) on the RHS of equation (3.6). The net result of this type of geochemical weathering is to increase the pH (since H^+ ions are used up), and to increase both Na^+ and HCO_3^- in solution, since the five sets of equations are linked. Equation (3.10) in isolation is a surface exchange reaction, and no solute accumulates in solution. Only by linking the consequence of equation (3.10) through to the dissolved CO_2 equilibria does surface exchange result in an increase in solute in solution. The additional CO_2 diffusing into solution results in the generation of new H^+ ions, which in turn exchange for base cations in the crushed mineral surface. This series of linked reactions continues, and only stops when, for example, the solution becomes saturated with reaction products.

Reactions between dissolved species are usually rapid, and the surface exchange of H^+ ions onto crushed rock for base cations is also relatively fast. The slowest stage in these five equations is the diffusion of CO_2 into and out of solution – this is also the reason why gassy drinks such as lager and carbonated soda water stay fizzy for some time. This is another aspect of open and closed systems with respect to gaseous CO_2. The water body may portray closed system characteristics if the rate of chemical weathering is more rapid than can be compensated for by the diffusion of new CO_2 into solution.

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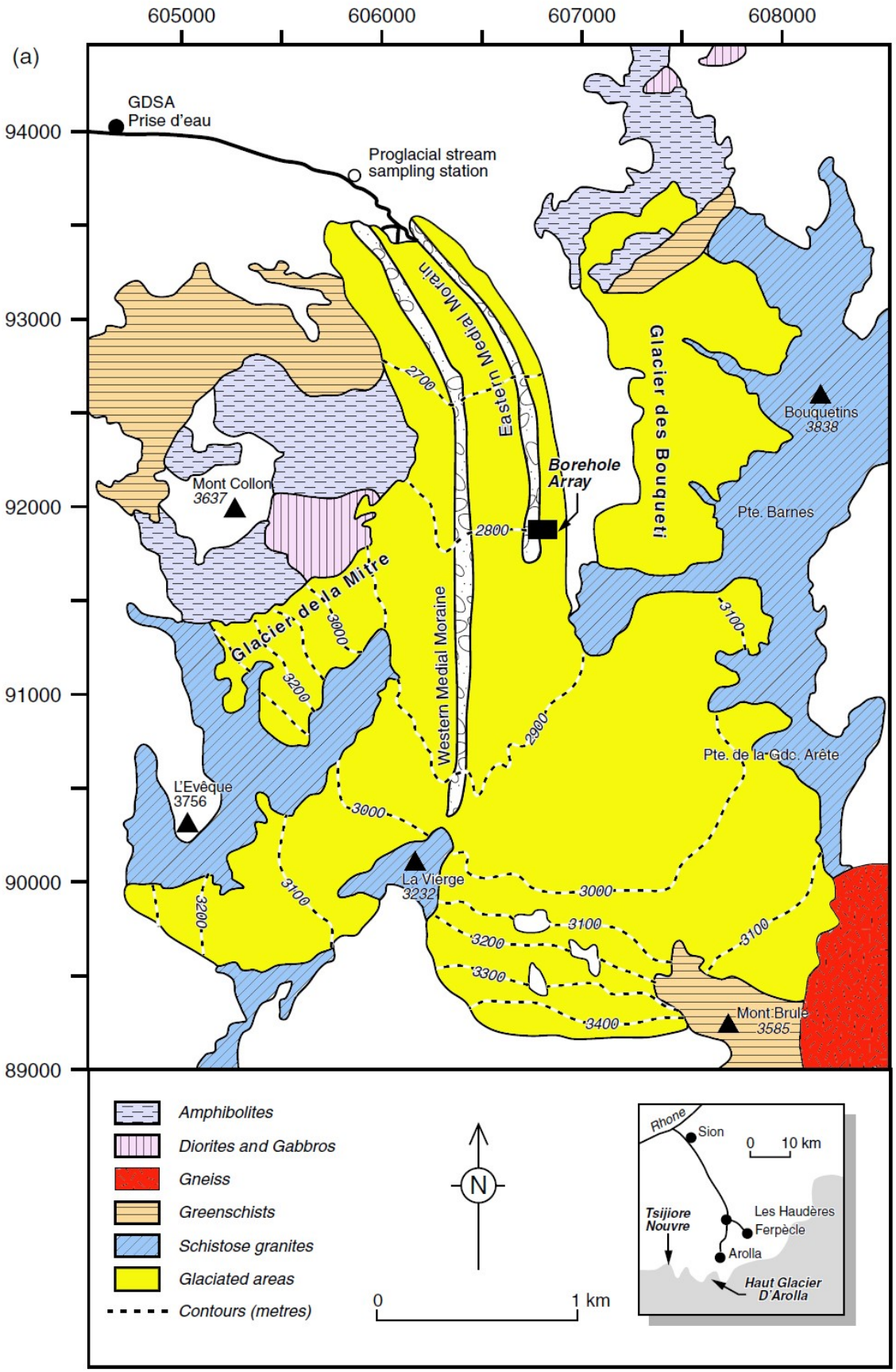
4. THE FIRST HAUT GLACIER D'AROLLA PROJECT (MT)

NERC funded a joint Cambridge-Southampton three-year project on "Integrated Approaches to Modelling Hydrology and Water Quality in Glacierised Catchments", which was focused on the Haut Glacier d'Arolla (HGA) in Switzerland. The idea was to monitor drainage system evolution by using changes in the hydrochemistry of the bulk meltwaters leaving the glacier, in tandem with an intensive programme of dye injections into multiple supraglacial streams and moulins that would provide a direct measure of water transit times though the glacier and their changes over a full melt season (Richards *et al.*, 1996).

HGA (Fig. 4.1) is small valley glacier located in Canton Valais in the Swiss Alps. It is warm-based, which means that the ice at the glacier bed is at the pressure melting point, and that water flowing at the glacier bed is likely to melt the surrounding ice slightly (Paterson, 1994). This is because there is some frictional resistance to water flow, which causes heating and melting, and because water flowing downhill warms slightly as potential energy is converted to kinetic energy. This helps to explain why most glacier water draining from Alpine glaciers is always a little above the freezing temperature, rather than at 0 ^{o}C.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La Vierge
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Haut Glacier
D'Arolla

Figure 4.1 The location and dimensions of Haut Glacier d'Arolla, showing the position of local data collection points (modified from Tranter *et al*., 2002).

The classical view of Alpine glacier hydrology (Fig. 4.2) was summarised very neatly by Röthlisberger and Lang (1987). Snow and ice melt on the glacier surface flows down glacier towards the terminus, mainly *via* supraglacial streams. These streams are often intercepted by crevasses or moulins, which funnel the flow of water to the glacier bed. For the first time, we wanted to test the hypotheses that (i) there were indeed two types of water flow path at the glacier bed that would give rise to very different travel times and dye return curves, and (ii) these water flow paths were linked to waters that were either rich or deficient in SO_4^{2-}. The idea of conducting dye tracing experiments on glacier drainage systems was not new, but conducting many injections from multiple injection sites across an entire glacier throughout the length of a melt season certainly was (Nienow *et al*., 1996).

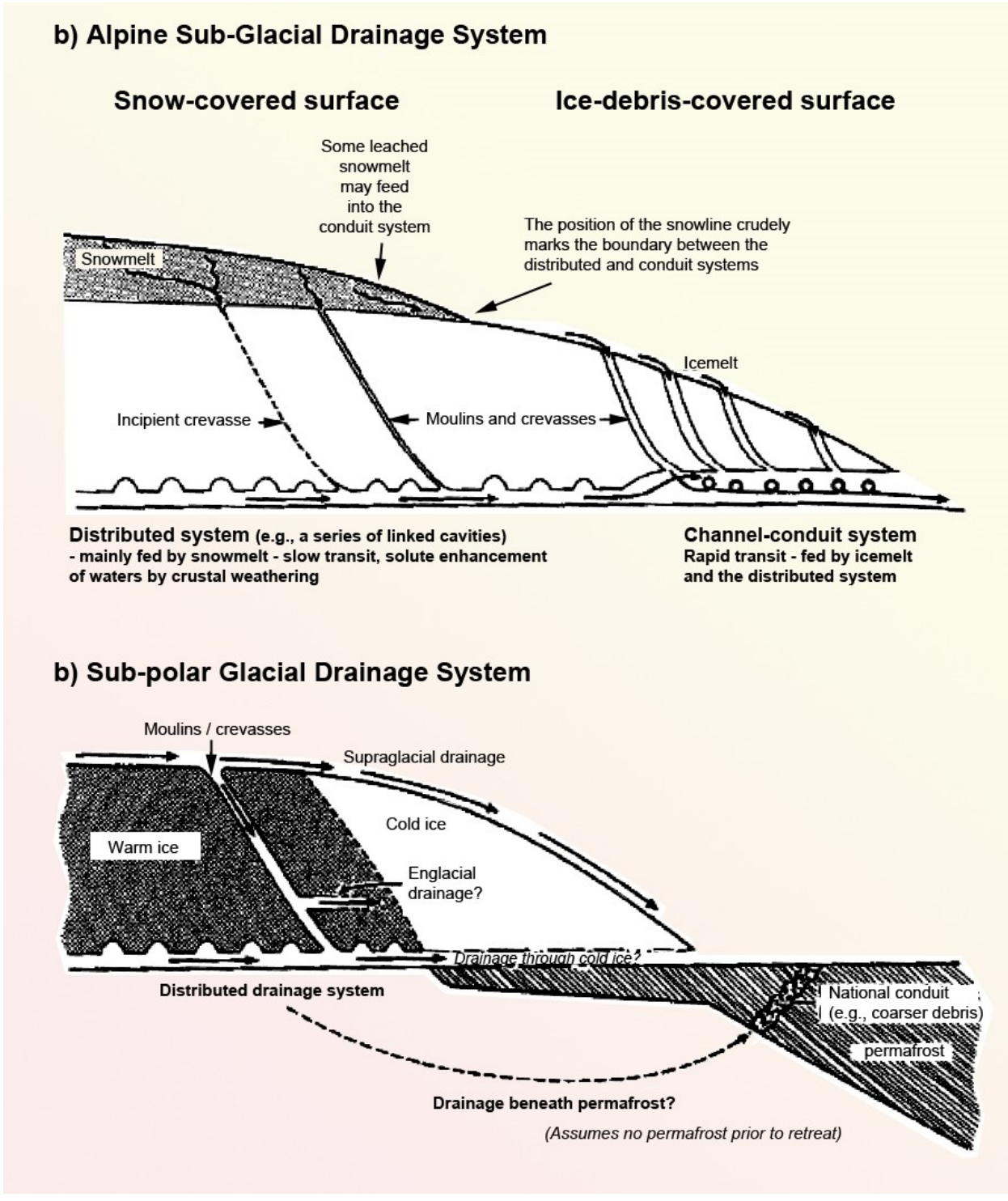

Figure 4.2 Schematic diagram showing the inferred structure of meltwater drainage systems of **(a)** Temperate Alpine, and **(b)** Sub-polar Glaciers (modified from Tranter *et al*., 1996).

4.1 Dye Tracing Experiments - A Learning Experience in Norway (MS)

Keith Richards, Ph.D. student Ian Willis, and I had started to conduct dye tracing experiments on Midtdalsbreen in Norway in 1985. Water flow through Midtdalsbreen turned out to be very

slow, with dye often taking tens of hours to reach the glacier terminus (Willis *et al*., 1990). We were working with a single dye (Rhodamine B), and this meant that there was a limit to how many experiments we could conduct in a season. We had to wait for all the dye from one experiment to come out of the glacier before we could start another experiment. As a result, we were limited to conducting one experiment every 2-3 days. We were also detecting the dye by manually collecting samples from the stream and pouring them through a fluorometer, which meant that someone had to sit by the stream for hours at a time to collect and run the samples. It was not a very efficient process and the weather made it a pretty unpleasant experience for whoever was on fluorometer duty. We learned a lot more about how not to run a dye tracing programme than we did about the glacier's hydrology, and we developed a false sense of how slowly water passes through a glacier.

4.2 Dye Tracing Experiments in the Alps (MS)

When we started work at HGA (Fig. 4.3) we quickly discovered that water passed through it much more rapidly through it than it did through Midtdalsbreen. This meant that we could conduct many more dye injections in a given period of time. HGA also offered many more potential dye injection points than Midtdalsbreen, so we could make injections along almost the whole length of the glacier. For a given distance from the glacier's terminus, it was often also possible to make injections at multiple points across the glacier. Overall, we used 47 different injection sites on the 6.33 km^2 glacier (Fig. 4.4a).

Up to 5 distinct streams emerged from the glacier terminus in a given melt season (Fig. 4.4b), which made it possible to investigate the catchment structure of the glacier drainage system by working out which injection sites resulted in dye emergence in which stream(s). It was the perfect site for using dye injections to investigate the behaviour of an entire glacier drainage system (Richards *et al*., 1996). In our first season at Arolla (1989), we conducted about 90 dye injections, focused on exploring how the dye travel time changed as injections were conducted progressively further up glacier, and on matching injection points to outflow streams.

Figure 4.3 Haut Glacier d'Arolla.

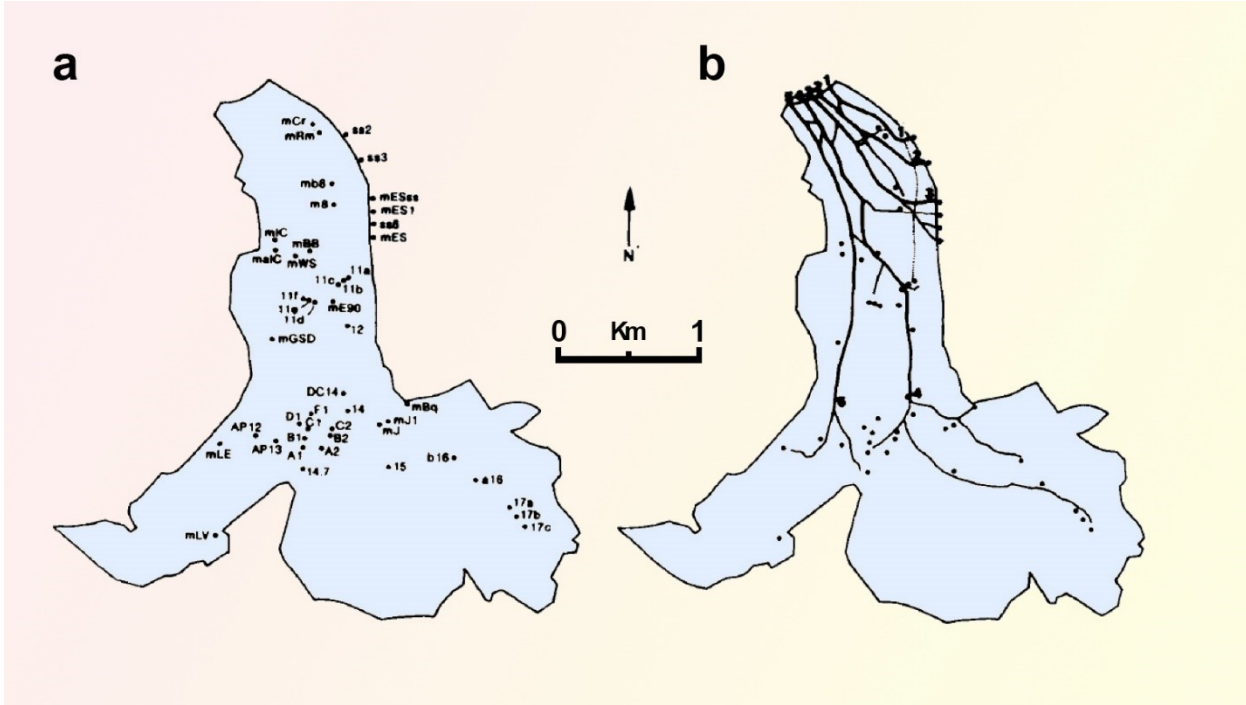

Figure 4.4 Maps of Haut Glacier d'Arolla showing **(a)** the locations of dye injection sites used in 1989 and 1990 (labelled dots), and **(b)** the subglacial meltwater drainage catchment structure inferred from the recovery patterns of dye recovery in each of the 5 meltwater streams emerging from the glacier. Some injection sites produced dye recoveries in more than

one stream, suggesting some degree of interconnectedness between the subglacial catchments (modified from Sharp *et al*., 1993).

In 1989, we started injections in July, by which time the snowline was quite far up-glacier and the subglacial drainage system was reasonably well established, especially at lower elevations on the glacier. We discovered that, at that stage of the melt season, there was already rapid drainage between input and outflow points over much of the lower glacier. We also found that there was a region near the head of the glacier from which drainage was appreciably slower. We determined that there were 4 definable supraglacial/subglacial drainage catchments feeding the 5 outflow streams. Using a combination of ground surveying and radio echo sounding of ice thicknesses, we were able to map the glacier's surface and bedrock topography, and to compute a hydraulic equipotential surface for the glacier bed (following Shreve, 1972). We used this surface as the basis for reconstructing the expected pattern of water flow over the glacier bed (Fig. 4.5), and compared the reconstruction with the catchment mapping based on the dye experiments (Sharp *et al*., 1993). The correspondence was surprisingly good and the results allowed us to design a more ambitious dye tracing programme for 1990 and 1991.

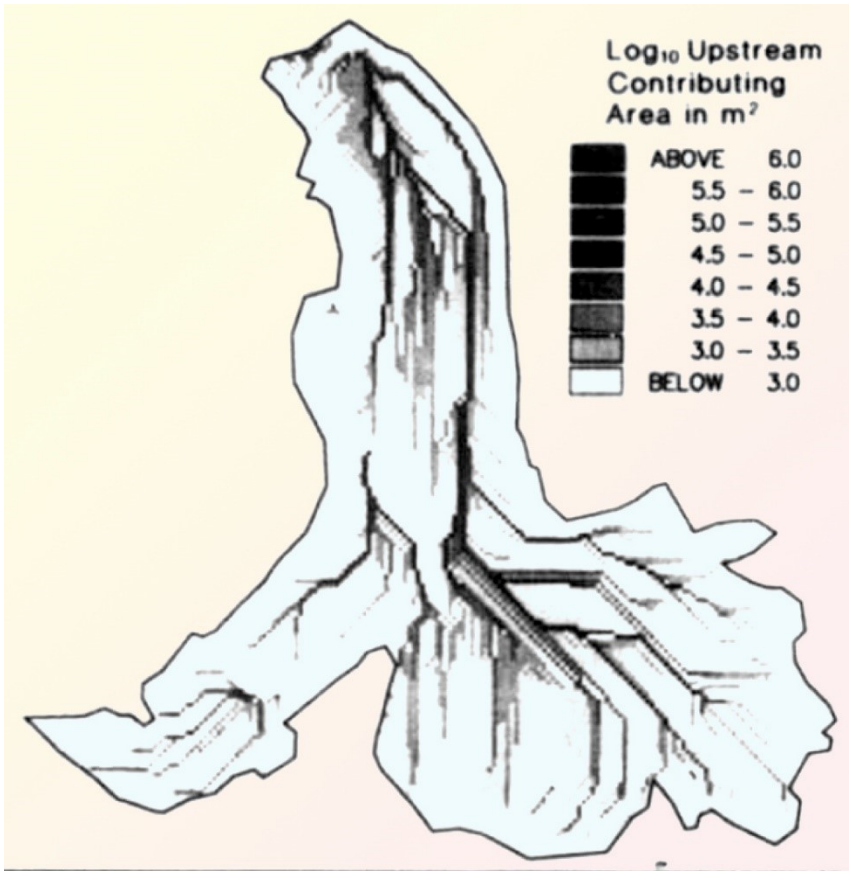

Figure 4.5 Theoretical structure of the subglacial meltwater drainage system of Haut Glacier d'Arolla, as reconstructed by assuming that water flow at the glacier bed is perpendicular to contours of subglacial hydraulic equipotential, which was computed following Shreve (1972) (modified from Sharp *et al*., 1993).

At this point, Peter Nienow returns to the story. Pete had been an undergraduate student in the second course that I taught after moving to Cambridge in 1984, and he had been in the field with us at Midtdalsbreen in 1985. After graduating, he had trained to be a teacher, travelled the world, worked for Thomson Holidays and, for some unfathomable reason, settled on becoming a Management Consultant. By 1989, he was having second thoughts and came to visit us in Arolla. The weather and scenery were stunning and we were having a lot of fun working there.

Pete was helping me with the dye injections. While walking up the glacier one day to start the day's injections, I made an off the cuff comment to the effect that this had to beat sitting in an office all day. The camel's back was broken - he agreed. We were able to get a NERC Ph.D. studentship for Pete later that summer and he came back to Arolla in 1990 to run the dye tracing programme. By then, we had realised that it would be both possible and desirable to conduct even more experiments than we had in 1989, so that is what we did. Subsequently, Pete and I went on to use the dye tracing methods developed at Arolla on much larger glacier systems in the Canadian Arctic (with Rob Bingham; Bingham *et al*., 2005, 2006) and Greenland (with Jemma Wadham; Chandler *et al*., 2013).

To conduct more injections in a season, we needed to use multiple dyes so that we could have more than one injection in progress at the same time. This meant we had to run two fluorometers, so we could detect the two dyes (Rhodamine B and Fluorescein) with different instruments. We wanted to run the instruments in continuous flow mode and attached to data loggers so as to reduce the need for manpower and manual data recording. However, the fluorometers still needed to be watched constantly so that the inevitable problems with maintaining the flow through them could be fixed immediately (thank goodness for the stream of Cambridge undergraduates who were ever-willing to help us with this – this brought Mark Skidmore and Jemma Wadham into the field, and you will hear more of them later). The increase in productivity and insight derived from these experiments was huge. We were able to conduct injections from mid-June until the end of August at sites located between 1 and 4 km from the glacier terminus, and to map the evolution of dye travel time across most of the glacier over the course of the melt season (Nienow *et al*., 1998).

We found that, for any given injection site located low down on the glacier, travel times early in the season were on the order of 5 hours, but that they decreased rapidly to 50 minutes or less by late June, after which they remained fairly stable (Fig. 4.6). The same pattern of change in transit times was repeated at injection sites located up to 3 km from the glacier terminus. However, since runoff was initiated later in the year further up-glacier, the transition from slow to rapid drainage occurred later, and the dye transit times became longer, the further the injection site was from the glacier terminus (about 150 minutes for injection sites located 3 km from the terminus). For injection sites further than 3 km from the terminus, however, transit times were much longer (up to 1,000 minutes or more), and they changed very little over the course of the melt season. The implications were that the "fast" component of the drainage system was largely absent from the glacier in the early part of the melt season, that it initially formed low down on the glacier, and that it extended progressively further up-glacier as melt became more extensive. The headward growth of the channels seemed to be linked to the increase in rates of meltwater production that occurred as the supraglacial snow cover (with its high albedo and significant water storage capacity) was removed, and glacier ice (with a much lower albedo and limited water storage capacity) was exposed at the surface. Once melt stopped, the drainage system was gradually shut down, presumably because empty or partially full channels at the glacier bed were squeezed smaller and smaller by deformation of ice into the empty channels (creep closure). This process seemed to be largely complete by the end of the winter.

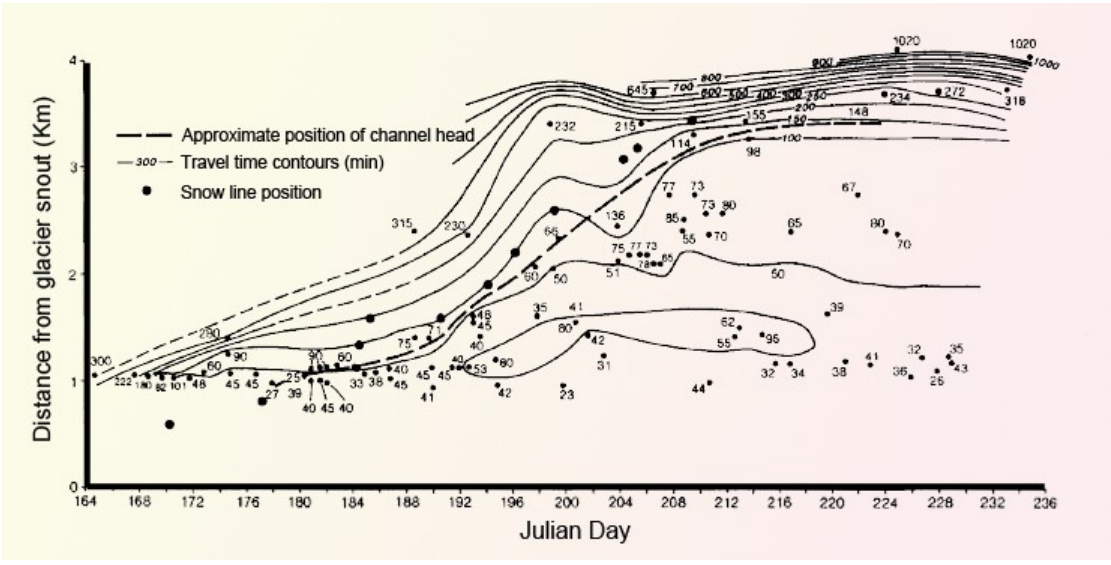

Figure 4.6 Time-space variation in dye travel time during the 1990 melt season at Haut Glacier d'Arolla. The seasonal growth of a rapid transit system in the lower 3 km of the glacier is apparent, and the approximate position of the conduit head and the transient snowline are also indicated (modified from Richards *et al*., 1996).

When we compared the upstream migration of the head of the region with rapid water flow in the lower glacier with the pattern of snowline retreat on the glacier surface, we found a very close coincidence (Nienow *et al*., 1998). This suggested to us that a difference in the degree of diurnal variability in the rate of runoff into moulins from surfaces that were snow-covered (very low diurnal runoff variability because of the capacity of the snowpack to store and delay the runoff of surface melt) as opposed to surfaces that were snow-free (very high diurnal runoff variability because of the limited capacity for water storage on sloping ice surfaces). We thought this might play an important role in driving the structural evolution of the subglacial drainage system over a melt season. We inferred that two processes could account for this behaviour: (i) the removal of the water storage capacity of the snowpack, which promoted more rapid runoff from the glacier surface during the day, and (ii) the reduction in surface albedo associated with the snow-to-ice transition, which increased the amount of meltwater being produced *per* unit melt energy available in snow-free areas of the glacier.

These hypotheses were subsequently tested and found to hold by the Ph.D. research of Ben Brock (Brock *et al*., 2000a,b) who explored the spatio-temporal evolution of the glacier's surface albedo and aerodynamic roughness length over the course of a melt season, and the post-doctoral work of Neil Arnold, who investigated the implications of these changes for the surface energy balance of the glacier and for surface melt rates and runoff (Arnold *et al*., 1998; Willis *et al*., 2002). From this work, we concluded that the primary drivers of seasonal changes in the efficiency of the subglacial drainage system were the increases in the magnitude and 'peakedness' of the diurnal meltwater input hydrograph to moulins that followed the removal of the snowpack from the glacier surface. We argued that these changes would generate very high transient water pressures and both longitudinal and transverse water pressure gradients in the subglacial drainage system at times of peak meltwater input. This would accelerate rates of water flow and energy dissipation at the glacier bed, drive the creation of well-defined meltwater channels by a combination of hydraulically forced separation of the glacier from its bed and channel growth by wall melting (Nienow *et al*., 1998), and perhaps also drive exchanges of water between the major drainage channels and surrounding areas of the glacier bed. The latter would be a potential mechanism for facilitating the mixing of water types characteristic of the meltwater channels themselves, and water types draining from areas of the bed with more distributed and less efficient drainage systems.

Superficially, these results might seem consistent with the underlying assumptions of the 2 component mixing model in that we recognised that the subglacial drainage system had two main elements (one characterised by slow flow and the other by fast flow), both of which were

fed by meltwater from the glacier surface. These elements were clearly connected as dye that passed through the slow system ultimately emerged from the glacier in the same channels as dye that passed through the fast system. Thus, waters from the 2 systems were certainly mixing before they emerged from the glacier. However, we suspected that the seasonal transition from long to short transit times that was demonstrated by dye traces from injection sites on the lower glacier did not mean that the slow drainage system in the lower glacier had been completely eradicated by the development of large meltwater channels at the glacier bed. Instead, it seemed more likely that the bulk of the surface meltwater was finding its way directly into the subglacial channel system and by-passing the slow system. This slow system was injecting more limited amounts of water (with a quite different chemistry) into the channels wherever and whenever conditions allowed.

We thought that once large channels existed, they would likely be characterised by very high water pressures during peak discharge periods, and that there were probably also large horizontal water pressure gradients between the major channels and the residual slow drainage system. Such gradients might drive water from channels into the surrounding, more distributed, components of the drainage system during peak discharge periods. In contrast, low channel water pressures during periods of low discharge might allow water to drain back into the channels from the distributed system. Such behaviour could readily explain the well-known diurnal variability in the solute concentration of glacial meltwaters. Diurnal variability would be expected if the waters draining into the channels during periods of low channel discharge had acquired significant amounts of solute while stored in the distributed system (Tranter *et al*., 1993). Thus, we envisaged a subglacial system with a combination of fast and slow elements, the balance of which varied over the course of a melt season and with distance from the glacier terminus.

Temporal variations in the drainage system structure, and in the relative water pressures in the fast and slow systems likely drove significant changes in the flow pathways followed by water that entered the glacier at different locations on its surface, at different stages of the melt season, and at different times of day. Such changes could be expected to affect the residence times of water in the glacier, and in the different components of the drainage system, and also the extent to, and processes by which, they would acquire solute as they passed through it. Mixing of waters characterised by different and continuously varying residence times and flow routings might be expected to result in a spectrum of water chemistries. Such heterogeneity could not be revealed by the study of the electrical conductivity of the waters alone. Nevertheless this heterogeneity might provide important insights into the characteristics of the different elements of the subglacial drainage system and their evolution in time and

space over the course of a melt season. Testing this hypothesis was a task for the water chemists.

4.3 Hydrochemistry (MT)

Giles Brown was THE perfect post-graduate water chemist, because he came from a physical geography background and could never be accused of biasing his chemical results by having a preconception of what the results should be. Giles spent two long field seasons at HGA, collecting at least two samples a day during most of June, July and August in both 1989 and 1990. He also undertook several intensive 24 hour sampling periods, collecting and filtering samples every hour. He measured pH immediately using a methodology that was specific for low ionic strength solutions, and calibrated his pH probes with low ionic strength buffers on a daily basis. All the samples were analysed for major cations and anions by ion chromatography, which had made great leaps in precision and accuracy in the previous five years. He rapidly acquired the most comprehensive hydrochemistry data set for glacial runoff in the literature to date (Brown *et al*., 1994, 1996; Brown, 2002) (Fig. 4.7).

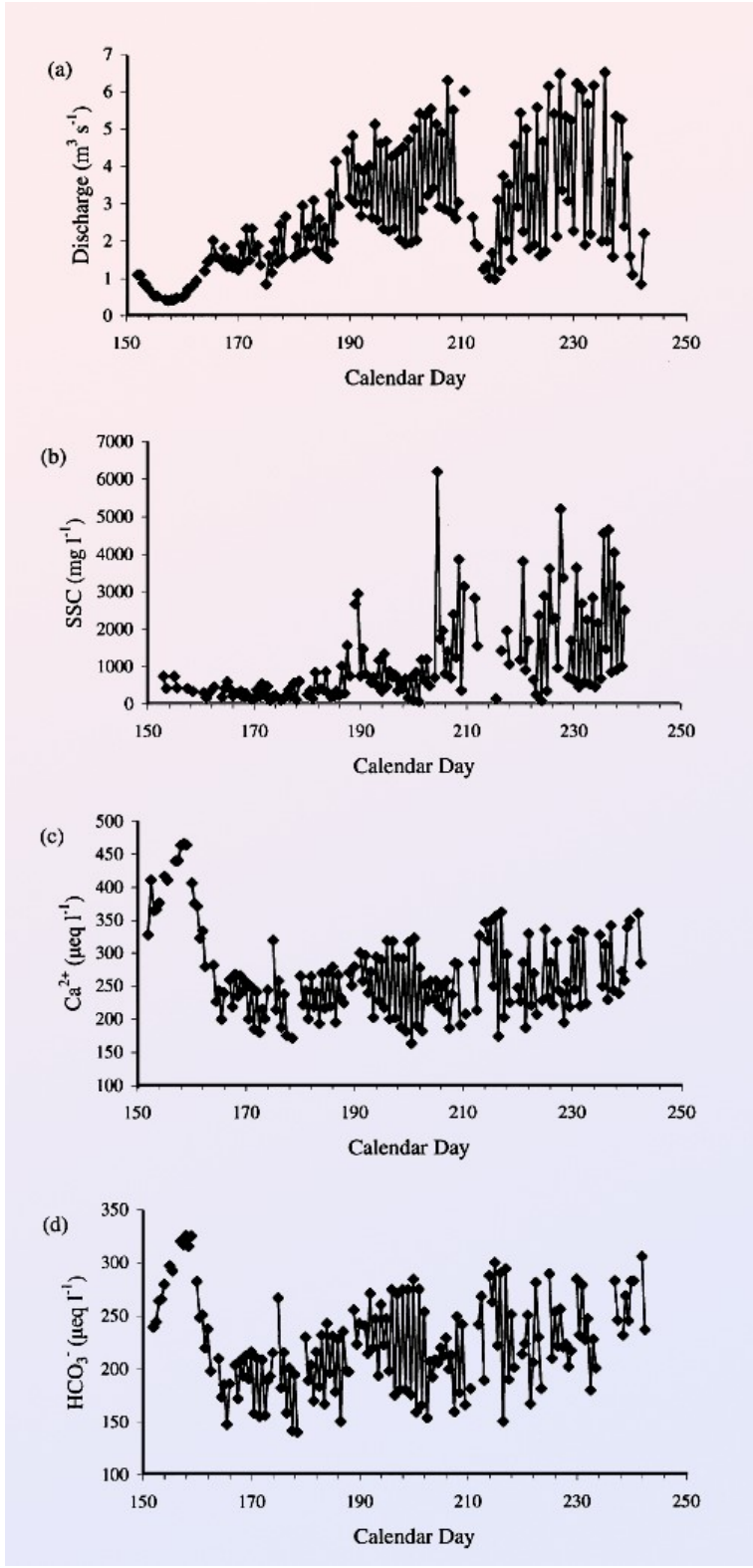

Figure 4.7 Variability in the hydrochemistry of Haut Glacier d'Arolla during June through August 1989 (Brown, 2002): **(a), (b), (c) and (d)** denote discharge, suspended sediment concentration, Ca^{2+} and HCO_3^- respectively. More variables can be found in the original reference (modified from Brown, 2002).

Fundamentally, the chemical characteristics of the runoff and their variations with discharge were similar to those we had found at Gornergletscher and Glacier des Bossons. Carbonation of carbonates and sulphide oxidation-driven carbonate dissolution (equations 2.4 and 3.5) were again the dominant subglacial chemical weathering reactions that we could infer from the composition of the runoff (Tranter *et al*., 1993). We were a little disappointed that we had not found something more surprising and/or different than before, but, on reflection, we were pretty pleased. Just about every type of bedrock contains trace quantities of carbonate and sulphide minerals, and crushing of bedrock is a characteristic of almost all glaciers, so it was very reassuring to find that chemical weathering beneath different glaciers in the Alps occurred in broadly similar ways. We began to think that sulphide oxidation linked to carbonate dissolution occurred mainly in the distributed component of the subglacial drainage system, since this is spatially pervasive, where crushed rock is most likely to first encounter water, and where water flow rates are relatively slow. As a result, there is more time for the coupled reactions to happen. We also felt that reactive sulphides were probably used up in the distributed drainage system, because there was scant evidence of them in suspended sediment (although small amounts of sulphide are difficult to detect). We thought that carbonation of carbonates was the main weathering process active in the channelised drainage system, though it probably also occurred in the distributed system. However, there were a few problems with this world view (Tranter *et al*., 1993).

First, sulphide oxidation is quite a slow reaction unless it is catalysed by microbes. Indeed, microbial oxidation of sulphides is the usual process in most near-surface Earth environments (Sharp *et al*., 1999; Torres *et al*., 2014). At the time, glaciers were thought to be largely abiotic, so the notion of microbially-catalysed sulphide oxidation underneath glaciers struck us as, frankly, barmy. Second, just how enough CO_2 and O_2 could access the glacier bed to help chemically weather the suspended sediment was difficult to understand. Some CO_2 and O_2 could be released from from gas bubbles in the ice during regelation around bumps on the glacier bed. Ice flow around such bedrock protrusions results in pressure melting on the up-flow side, and refreezing of the water on the down-flow side. Gases are largely excluded from refreezing water (Hallet, 1976b). However, our calculations suggested that a regelation source of CO_2 would not be a large, based on the thickness of the basal regelation ice layer and its annual movement. We suggested that CO_2 was perhaps entrained in meltwater as bubbles as waters drained into the glacier *via* moulins, and that atmospheric gases might invade subglacial channels in the vicinity of the glacier terminus at low flow. The former was special case pleading, which is never a comfortable position to hold, and it was difficult to see how atmospheric gases could invade too far up-glacier from the terminus. This made carbonation in the channelised drainage system difficult to sustain as a pervasive process beneath

glaciers. The low pCO_2 of runoff at high discharge is testimony to the lack of CO_2 sources in the channelised drainage system (Tranter *et al*., 1993).

We were also confident that suspended sediment exiting the bed of HGA in runoff (Fig. 4.7b) was geochemically reactive (Brown *et al*., 1996). Giles conducted a series of "holding" experiments. He sampled turbid glacial runoff, but left it unfiltered and in contact with the atmosphere, standing the samples in calm side waters to keep them at *in situ* temperature. The conductivity of these unfiltered samples increased over time, showing that the dilute meltwaters continued to react with the suspended sediment. Analysis of the samples showed that Ca^{2+} and HCO_3^- were the ions that increased in concentration, so carbonation was occurring. These experiments were important for two reasons. First, the capacity for the suspended sediment to react with dilute meltwaters was not exhausted as long as a supply of CO_2 was present. Second, this was another big problem for the 2CCMM. Post-mixing reactions were occurring, increasing the conductivity of more dilute meltwaters in particular. So, given time and a subglacial source of CO_2, chemical weathering by carbonation could occur in the channelised drainage system, contrary to the assumptions of the 2CCMM (Sharp *et al*., 1995a).

Another significant problem for the 2CCMM was that when we used SO_4^{2-} to separate the hydrograph over the ablation season, the SO_4^{2-} concentration we calculated for the subglacial water component appeared to vary (Brown, 1991). The method we used was empirical (Tranter and Raiswell, 1991), and not very rigorous, but it was the best I could come up with at the time. Further, when we used different ions to separate the hydrograph, we got very different results depending upon which ionic species was used in the calculation (Brown *et al*., 1996) (Fig. 4.8). It took some of the most animated discussions between Martin and I for me to finally accept that the 2CCMM was not fit for purpose. The subglacial environment was too dynamic and heterogeneous for this descriptive tool to work in detail – it was just too simple a solution for too complex a problem.

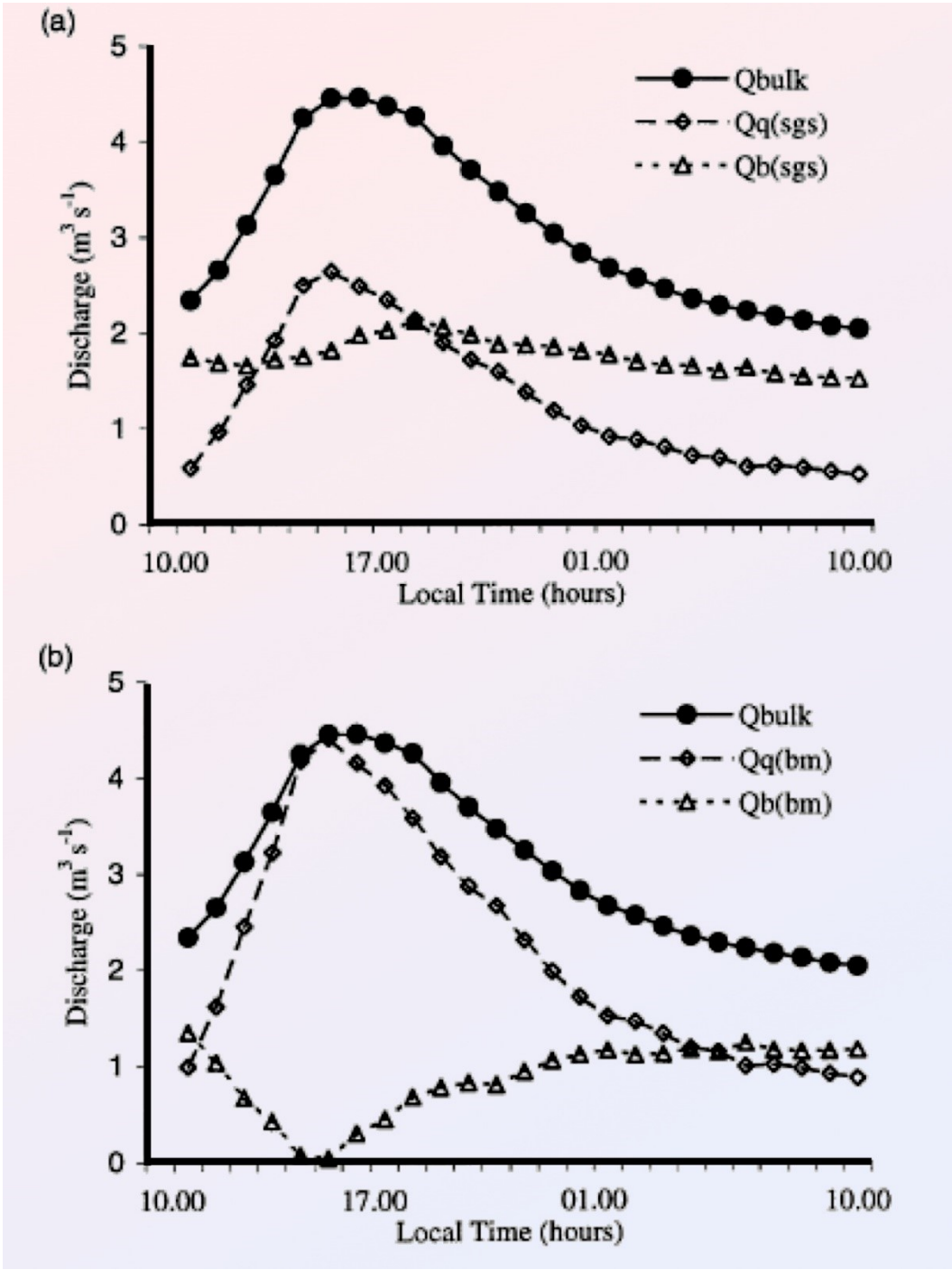

Figure 4.8 Hydrograph separation of bulk meltwaters draining Haut Glacier d'Arolla on 17th and 18th July 1989. The hydrographs were separated assuming that the Ca^{2+} concentration of the englacial component is either that of the most concentrated supraglacial meltwater sampled (16 µeq L^{-1}) or the season's minimum value (165 µeq L^{-1}). The Ca^{2+} concentration is assumed to be 340 µeq L^{-1} (modified from Brown *et al*., 1996).

The end of the first Arolla project put us in the position of having inferred the principal flow paths and chemical weathering reactions under HGA from an examination of the runoff chemistry. Martin was determined to test these hypotheses by drilling to the bed of the glacier and sampling the waters directly. He wrote a great grant application to NERC, stressing the need for a step jump in the way that research into glacier hydrology and hydrochemistry was conducted, which in turn would produce a step jump in understanding of subglacial water flow paths and geochemistry. NERC funded us. Giles applied for a NERC fellowship at the same time, and was also funded, and moved to Cambridge to undertake experimental work on the chemical weathering of subglacial sediments. We were about to embark on quite a journey of discovery. The second phase of the Arolla Project would fundamentally change the way we thought about chemical weathering at the glacier bed.

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5. THE SECOND AROLLA PROJECT (MS)

The new drilling project brought several talented students into the field. Bryn Hubbard had just completed his Ph.D. in Cambridge with Martin on the characteristics of basal ice in Alpine glaciers, and he became the lead driller on the project, while Michael Nielsen was our drilling and instrument technician. Bryn was subsequently hired into the Centre for Glaciology at Aberystwyth, which he now directs, as was Giles Brown. Shulamit Gordon, a Bristol undergraduate, went on to do her M.Sc. with Martin in Alberta on borehole water quality profiling, and then worked on drilling projects with Barclay Kamb and Hermann Engelhardt in Antarctica, before ending up in New Zealand and working as a science advisor and logistics co-ordinator for Antarctica New Zealand. Jemma Wadham, then a Cambridge undergraduate, did her Ph.D. with Martyn on the chemistry of glacial meltwaters in Svalbard and became a faculty member in Bristol, from where she has made key contributions in the field of glacier biogeochemistry.

We needed to drill to the bed of HGA to test and develop the ideas on subglacial drainage system behaviour that were emerging from the first Arolla project, but we lacked the expertise to do this. Chris Smart, a karst hydrogeologist based at the University of Western Ontario in Canada, was pioneering the use of hot water to drill rapidly through shallow ice (up to a few hundred metres), and he agreed to act as a consultant in our design and use of a hot water drill. He trained us in drilling techniques at Small River Glacier in British Columbia in July 1993, and then joined us in Arolla for our first drilling season that August/September. Chris's students Ginny Catania (now a glaciologist at UTexas, Austin), Brad Ketterling, Steve Head, and Keith Carr also joined us for that season. Chris's previous experience with drilling at Small River Glacier (and Trapridge Glacier in the Yukon) influenced the way we approached drilling at Arolla.

Chris clearly understood that borehole water levels could fluctuate over time in many different ways. He therefore classified boreholes on the basis of their minimum recorded, or base, water level, and of the amplitude of their diurnal water level fluctuation during the melt season. He described base water levels as dry, low standing or high standing, and fluctuation amplitudes as zero, low or high (Smart, 1996). Thus, we potentially had nine borehole types, but not all of these actually occurred. High-standing boreholes with no diurnal variation in water level were considered to be "unconnected" to an active subglacial drainage system, whereas all others were considered to be "connected" to such a system.

Chris thought that it would be possible to identify spatial structure in the distribution of borehole types with a well-designed array of multiple boreholes, and that that would help us understand

the configuration of the subglacial drainage system - albeit in a relatively small area of the glacier. Spatial structure in the temporal variability of borehole water levels (and in the variability of horizontal water pressure gradients that was implied by changing water level differences between adjacent boreholes) could potentially inform us about how different elements of the subglacial drainage system interacted with each other, and how these interactions evolved over time both seasonally (as the summer drainage system formed and decayed) and diurnally (as water inputs to the system varied over time).

Chris also advised us on drill design. Our drill was fed by a hot water stream produced by a portable car wash system. This was fed by supraglacial melt water that we collected in a reservoir on the glacier's surface. The car wash heater produced a pressurised water stream with a temperature of ~90 °C. This was fed into an insulated high-pressure hose that was connected to a stainless steel drill stem with a brass drilling tip (see Fig. 5.1).

Figure 5.1 Hot water drilling at Haut Glacier d'Arolla in 1993.

The drill produced a jet of hot, pressurised water which, when directed vertically at the ice surface, produced a hole. As the hole developed, the drill stem and hose were lowered down into it and the hole gradually became deeper, eventually reaching (in most cases) the glacier bed (at a depth of between 50 and 140m, depending on location). At this point, the drill stopped descending further into the ice because it hit the underlying bedrock or sediment below). The hose was looped over the shoulders of the driller so that it could be lowered into the hole at a controlled rate. This relatively simple technology enabled us to sink boreholes down to the bed of HGA. There were a few surprises when the water column in a hole drained abruptly when the drill reached the bed and the weight of the whole system was instantly transferred to the

driller. In the worst case, an unsuspecting assistant who was walking away from the borehole with the hose looped over their shoulder in order to pull up the drill might find themselves suddenly flat on their back! However, by and large, the system worked very well. Once we had a hole that reached the bed we could send water sampling devices down (Fig. 5.2), and install instruments within or at the base of the hole. We could also inject tracers directly into the subglacial drainage system from the base of the hole. In theory, this allowed us to measure water flow velocities in the subglacial drainage system alone, without the complication of an initial phase of vertical flow through the body of the glacier.

Figure 5.2 Our first down-borehole water sampler.

5.1 Boreholes and Physical Measurements

5.1.1 Predicting the distribution of subglacial drainage pathways

Most previous hot water drilling projects designed to investigate subglacial hydrological processes had drilled boreholes along glacier centrelines in the ablation area, and most had apparently failed to intersect anything that looked like a major drainage channel. We had made four theoretical reconstructions of the subglacial drainage structure (Fig. 5.3) using our knowledge of the surface and bedrock topography of HGA (Sharp *et al*., 1993). Two of these (b and d) assumed that water in subglacial channels was at atmospheric pressure, in which case the pattern of water flow was dictated by the local slope of the bedrock. The other two (a and c) assumed that water flow was also influenced by gradients in ice thickness (and therefore ice pressure). We routed water across the glacier bed according to the magnitude

of the local gradient in hydraulic potential (determined by the local elevation head for cases where the water was assumed to be at atmospheric pressure, and by the sum of the elevation head and the additional head due to the weight of the overlying ice for cases where it was assumed to be pressurised by the ice).

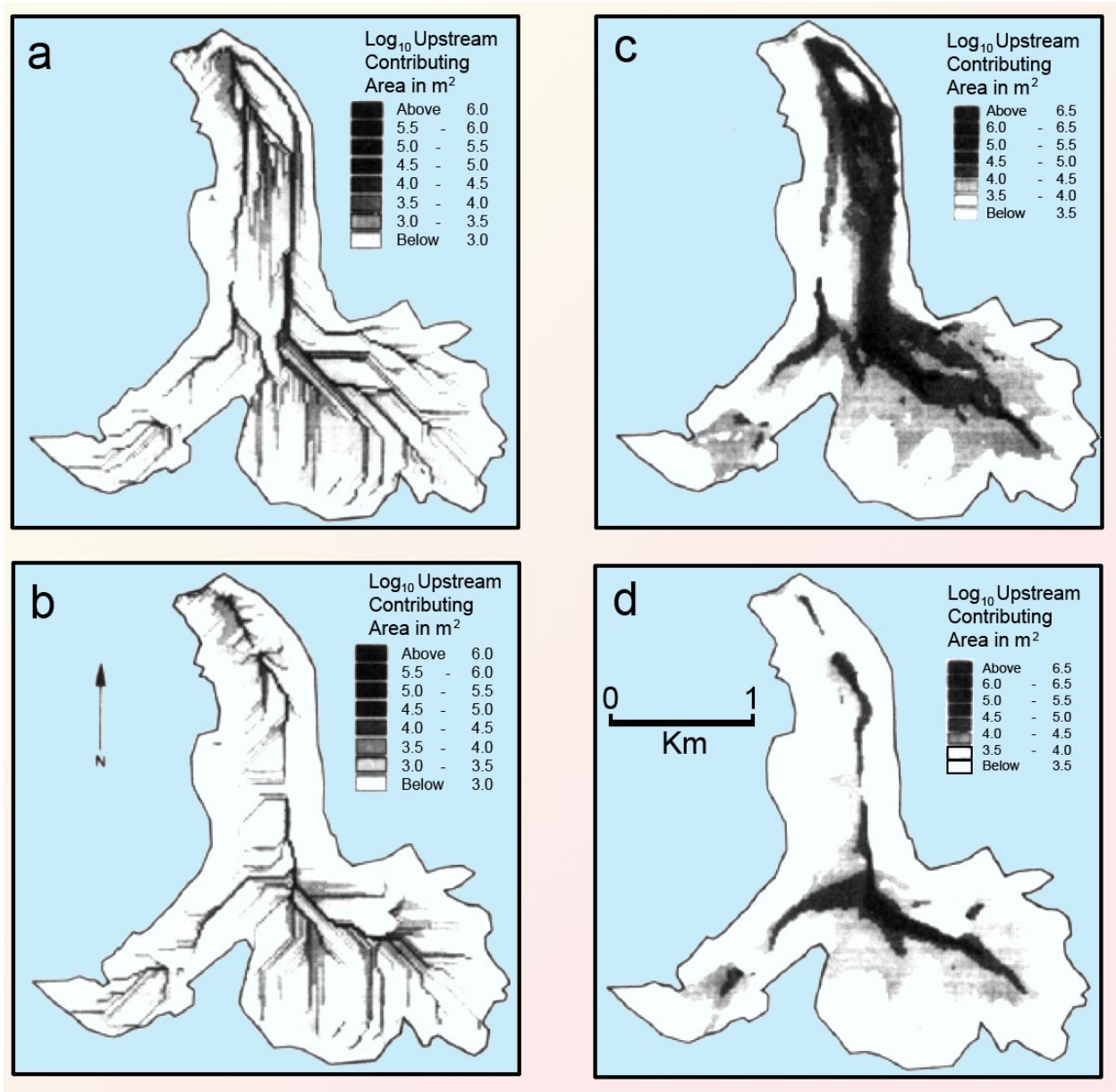

Figure 5.3 Reconstructions of the subglacial drainage system of Haut Glacier d'Arolla based on (**a,c**) $\log_{10}$ upstream area for gridded values of subglacial hydraulic potential, (**b,d**) $\log_{10}$ upstream area for gridded values of bedrock elevation. Reconstructions (a) and (b) assume that each grid cell passes area only to the adjacent cell with the lowest potential or elevation, while (c) and (d) allow area to be passed to all adjacent cells with lower potentials or

elevations, in proportion to the magnitude of the gradient of elevation or potential between cells.

As flow routing was calculated using gridded datasets, each cell could potentially receive water from, or deliver water to, any combination of up to 8 surrounding grid cells. For each case, we performed 2 reconstructions – one that assumed water leaving a given cell was routed to the single adjacent cell with the lowest calculated hydraulic potential (a and b), and another (c and d) that assumed that it was routed to all cells with hydraulic potentials lower than that of the source cell, but in proportion to the magnitude of the hydraulic potential difference between the source and receiver cells. In the first case, flow became concentrated in the deepest part of the valley and only a single stream emerged at the glacier terminus. In the second case, the reconstruction generated at least three significant streams beneath the ablation area of the glacier (which combined into a single stream very close to the terminus), and as many as seven beneath the accumulation area.

5.1.2 Designing a borehole array

The drainage reconstructions for which the ice pressure affected the subglacial hydraulic potential (Figs. 5.3a,c) seemed to match our reconstruction of the subglacial stream network that was based on dye injection results (Fig. 4.4b) much better than those that assumed the ice pressure was not important (Fig. 5.3b,d). Thus, we used the former reconstructions to choose a location for our drilling site. This was located towards the eastern margin of the glacier in its ablation area, a location where the reconstructions suggested there should be major drainage axis. This turned out to be a good call and it did not take too long to locate an axis along which borehole water levels were relatively low compared to surrounding areas, which we took to indicate that we were fairly close to a major stream at the glacier bed (Hubbard *et al*., 1995).

5.1.3 Uses of boreholes

We intended to use our boreholes to make direct injections of dye at the glacier bed, so that we could measure water transit times from the drill site to the glacier terminus, and how these varied through a day. We also wanted to instrument the boreholes to measure water pressure, water temperature, electrical conductivity, and turbidity at the glacier bed over the course of a melt season, and ideally through the winter. This would allow us to explore how the system

opened up in spring, functioned during the summer, and shut down in the fall and winter. Another goal was to extract water samples directly from the base of boreholes. This would allow us to explore how the water chemistry varied across the bed as a function of location relative to the channel, and how it changed over time in different parts of the bed. Once we actually had boreholes to work with, it soon became apparent that they quickly became an active part of the glacier drainage system as they remained open to the atmosphere for most of the melt season. This allowed meltwater from the glacier surface to enter the boreholes from above if they were not completely full. Water could also enter from the bottom of the hole if subglacial water pressures exceeded the pressure attributable to the height of the water column in the borehole. If the boreholes intersected englacial channels or open fractures, then water could also enter and leave the borehole through its walls (Gordon *et al*., 2001).

5.1.4 Borehole hydrology

The situation was sufficiently dynamic that we concluded there would be value in trying to study the hydrology of the boreholes themselves. We approached this using a combination of *in situ* measurements of water level and the electrical conductivity and turbidity of waters at the base of the holes, water sampling from hole bases, and repeat measurement of the vertical electrical conductivity profile of the borehole water column (Gordon *et al*., 1998, 2001). This allowed us to detect new water types entering and leaving the borehole base, and track their movements up and down the borehole as water levels fluctuated. It also gave us a good sense as to whether water level increases resulted from increasing water fluxes into the borehole from the surface or sides, or from increasing pressures in the subglacial drainage system (or the reverse for falling water levels). We also discovered that there could be water exchange between boreholes and the body of the glacier *via* fractures and micro-channels that intersected the borehole walls. Understanding this behaviour was critical to interpreting sensor records from the bases of boreholes in terms of changes in the relative importance of water inflow and outflow at the borehole base, *via* the borehole walls, or at the surface. Having a relatively dense array of instrumented boreholes turned out to be essential to understanding how the system as a whole was behaving as we detected spatially propagating signals that were previously unrecognised.

5.1.5 1993 Field season – a variable pressure drainage axis

In our first field season in 1993, we drilled an array of 24 boreholes around the suspected subglacial drainage axis at a location about 1.5 km from the glacier terminus. Mapping of the

daily minimum water level and the amplitude of the diurnal water level variation in these boreholes clearly showed that, by mid-August, there was a well-defined axis a few tens of metres wide that cut across the array. Within this axis, the daily minimum water levels were much lower than in areas on either side of it, and the amplitude of the diurnal water pressure fluctuation was much higher. We referred to this as a "Variable Pressure Axis" (or VPA) and concluded that it marked the location of a major subglacial drainage channel fed by supraglacial runoff (Hubbard *et al*., 1995).

Monitoring of the temporal evolution of the water level field within the borehole array showed that there was a diurnal reversal in the direction of the water level gradients on either side of the VPA. Gradients away from the axis increased as water levels within the axis rose to their daily peak, while they decreased and eventually reversed as axis water levels fell to their daily minimum. This strongly suggested that the channel that occupied the VPA was exchanging water with adjacent areas of the glacier bed over the course of the diurnal runoff cycle. Water would leave the channel during periods when water levels within the VPA were high and/or rising, and return to it when VPA water levels were low and/or falling. Changes in the turbidity of water at the bases of the boreholes suggested that these flows were able to mobilise fine sediment from a sediment layer beneath the glacier.

The rate of propagation of the diurnal water pressure peak away from the VPA seemed to slow with increasing distance from the VPA, perhaps suggesting that the inferred water flows to and from the channel were removing fine material from subglacial sediments near the channel thereby increasing their hydraulic conductivity and decreasing the resistance that they offered to water flow and pressure wave propagation. It also seemed possible that this process created conditions favourable for in-stream weathering of fine grained subglacial sediment. If that proved to be the case it would be a clear challenge to the assumptions underlying interpretations of subglacial drainage system behaviour based upon the application of the 2 component conservative mixing model.

Somewhat to our surprise, we found that at least some of the boreholes became an active part of the glacier drainage system. We observed that subglacial water could enter the base of the boreholes and rise up them, sometimes escaping through fractures or micro-channels that intersected the borehole wall, and sometimes draining back down again as basal water pressure fell. This complicated the interpretation of both *in situ* measurements at the base of the boreholes and the chemistry of waters sampled from the borehole base.

We clearly needed to understand the hydrology of each and every borehole and how it was affected by water exchanges with the glacier bed, glacier body, and glacier surface if we were to make sense of the variability we observed with the sensors. To do this, we developed the

technique of repeat profiling of borehole water quality (electrical conductivity and turbidity) as a means of tracking the sources, movements, and sinks of distinctive packets of water that were moving into, through, and out of the boreholes. We also did some direct tracing of water movement by injecting salt into the borehole water column and following its movement over time. This became the focus of Shulamit's Master's thesis at the University of Alberta.

5.2 Borehole Hydrochemistry (MT)

Giles, now at Cambridge on a NERC Fellowship, looked after the runoff chemistry, and Helen Lamb, a Bristol Geography undergraduate, became our new Ph.D. student, working on the geochemistry of borehole waters. Mike Nielsen, the drilling and instrument technician on the project, designed a simple borehole water sampler that was similar to the Niskin bottle used in oceanography (see Fig. 5.2). It was pretty exciting sending the sampler down the borehole and collecting the first subglacial water sample from the bottom of HGA. Bryn Hubbard took me to a borehole near to what we thought was the VPA, we lowered the water sampler down the hole until we were at the bed. We raised the sampler off the bed by about 10 cm, then attached a weight (known as the “traveller”) to the rope and let it fall. The weight hit the sampler, triggered the closure mechanism and we pulled the sampler up. I was knocked out – the water was very turbid and had the greenish tinge of crushed meta-basic rock. It was an exciting moment, and I took a shot of Bryn holding the world’s first directly sampled subglacial water sample for posterity (see Fig. 5.4). Helen, Giles and I sampled waters from the base and within the water column of the borehole over the next three weeks.

Figure 5.4 Bryn Hubbard holding our first subglacial water sample, 1993.

We were monitoring the conductivity of water at the base of the boreholes, and also vertical conductivity profiles of the borehole water column, and we tried to sample concentrated waters that were rising up the borehole as basal water pressures increased, so maximising our chances of sampling true waters that were flowing at the glacier bed. Observations in the field appeared to paint a chaotic picture of conductivity variations, which was, on the one hand, very frustrating, since we thought we had the chemical weathering reactions and flow paths at the bed all understood, but on the other hand, it is a huge part of the fun of fieldwork to have one set of simple ideas and hypotheses overturned by much more complex, real world data. We sampled what and when we could from the boreholes, and trusted that we could collectively make sense of our data when we got back from the field.

Helen worked diligently analysing the water samples, and her hard work paid off handsomely. Her results were better than we could have imagined (Tranter *et al*., 2002). There were three groupings of samples (Fig. 5.5), evident when plotting individual ions against dissolved Si (hereafter Si). These three water types showed different types of borehole connections to the subglacial drainage system. It was a very exciting period - the data sets which had appeared so disparate in the field took on a coherence that we all felt sure would place our work at the leading edge of the field. Helen was rushed off her feet generating data and I was on study leave, so she kindly let me sit at home for a few weeks to work through the data and see if I could come up with a summary of what was happening geochemically at the glacier bed. I rejected data from unconnected boreholes, which were those holes in which the EC stratigraphy did not move through the day when water pressures were fluctuating. We only used data from samples collected as concentrated waters flooded into the base of the boreholes, giving rise to a basal plug of concentrated waters that grew larger as diurnal discharge and basal water pressures grew. This gave us most confidence that we were sampling waters that were representative of those flowing in the subglacial drainage system.

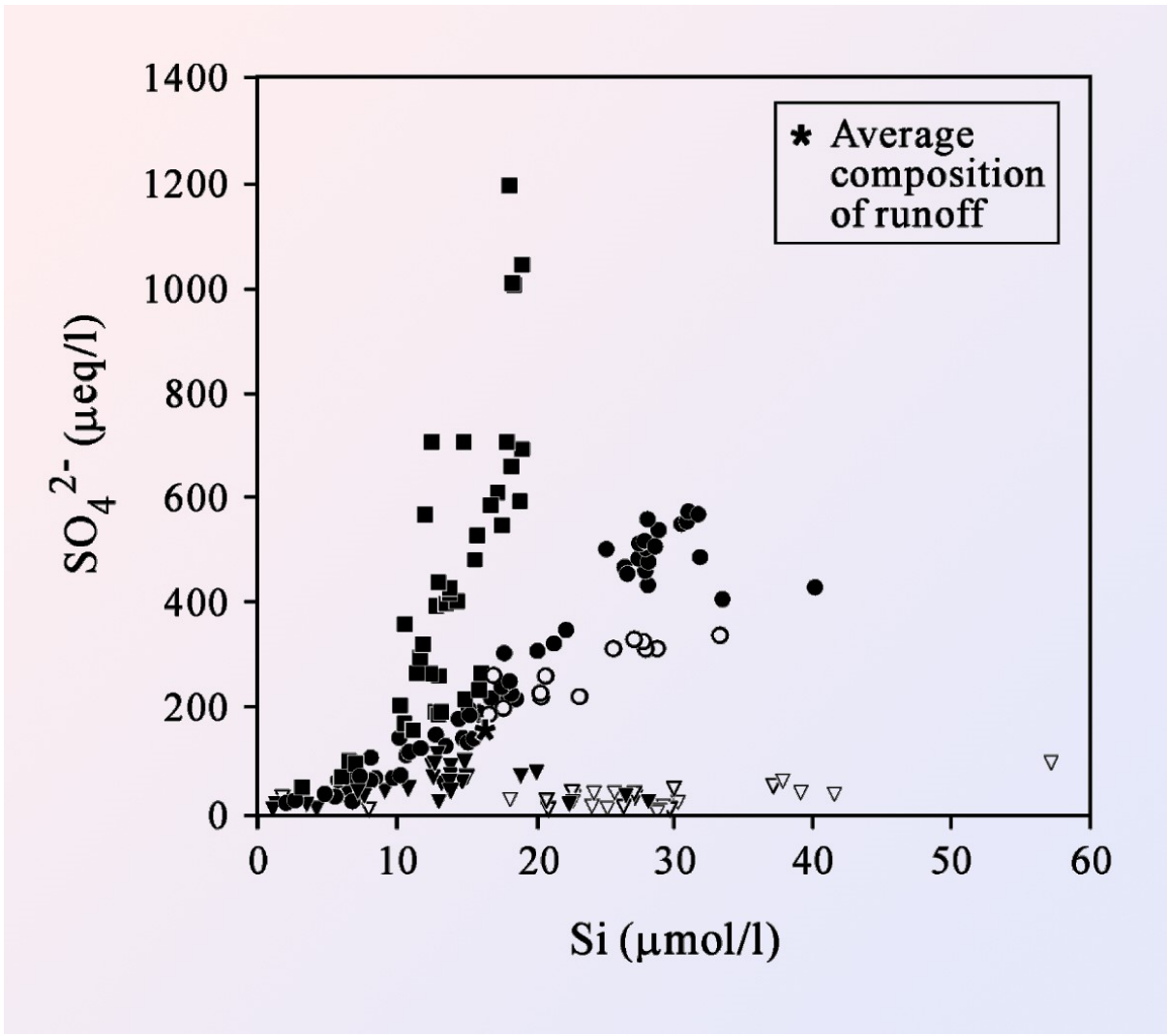

Figure 5.5 A scatter plot of SO_4^{2-} *versus* dissolved Si in borehole waters sampled from the base of Haut Glacier d'Arolla (modified from Tranter *et al*., 2002).

The most instructive scatter plot geochemically was HCO_3^- *versus* SO_4^{2-} (Fig. 5.6). I noticed that there was a linear association when SO_4^{2-} was greater than ~100 µeq L^{-1}, and that there was a non-zero intercept on the HCO_3^- axis of ~250 µeq L^{-1} (it was actually ~220 µeq L^{-1}). This triggered a memory of reading Garrels and Christ (1965) as a graduate student - it was the amount of alkalinity that arises when calcium carbonate dissolved in deionised water in a closed system, out of free contact with the atmosphere. I also remembered Giles Brown telling me that he had found this amount of dissolved bicarbonate in deionised water at 0 ^oC in a capped litre bottle a little while earlier, and I regret that I told him that he must have had a leak in the bottle, which must have allowed an ingress of air - more fool me for ignoring real world data.

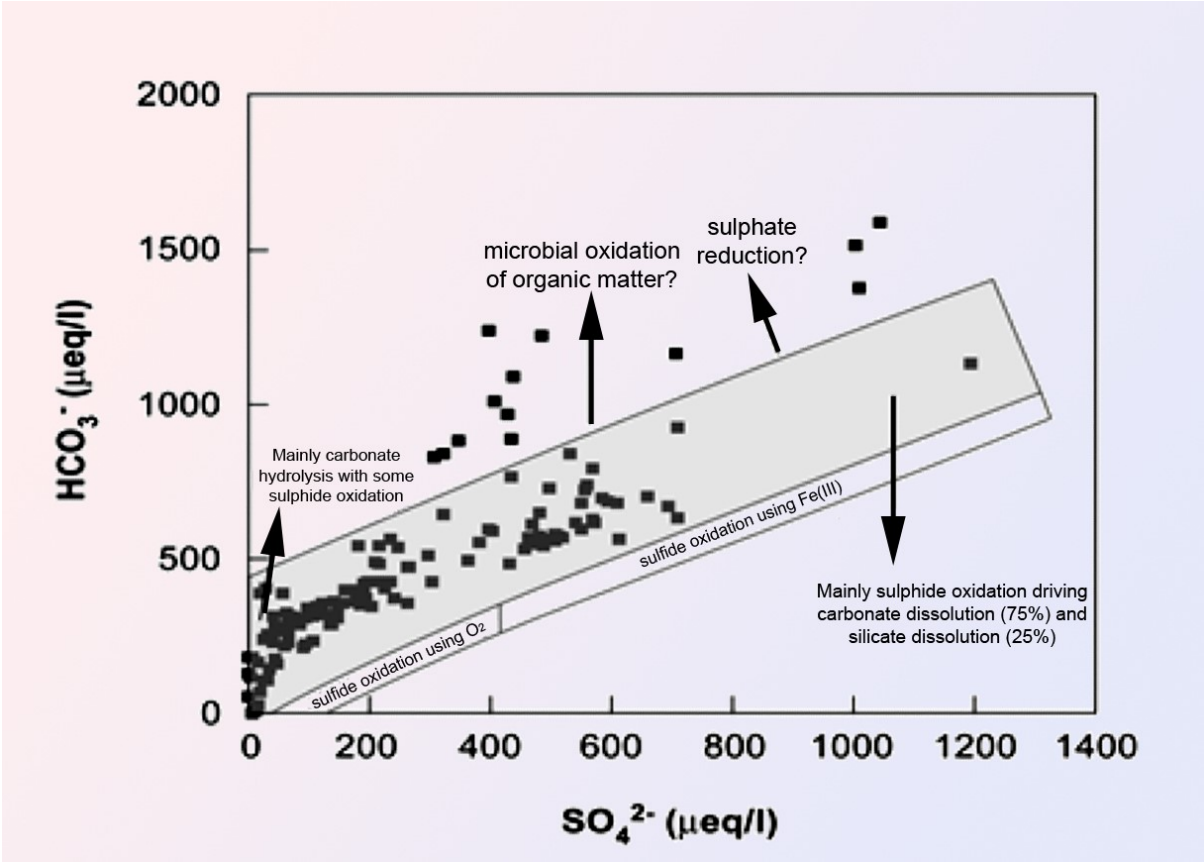

Figure 5.6 A scatter plot of HCO_3^- *versus* SO_4^{2-} in borehole waters sampled from the base of Haut Glacier d'Arolla (modified from Tranter *et al*., 2002).

There was a similar story for scatter plots of (Ca^{2+} + Mg^{2+}) *versus* SO_4^{2-}, where again the intercept was ~250 µeq L^{-1}. I grouped Ca^{2+} and Mg^{2+} together, since Mg^{2+} is a trace component of many calcium carbonate minerals, but I will just refer to "Ca^{2+}" for this section to keep explanation easier. Ca^{2+} and HCO_3^- were being released into solution in almost the exact concentrations one would calculate for carbonate hydrolysis at ~0 °C. Hence, carbonate hydrolysis (equation 2.4) was the first reaction that occurred when glacial flour encountered dilute meltwater at the bed of HGA. This is a rapid reaction, which only needs a carbonate mineral surface to be in contact with water. The reaction slows as the water approaches saturation. The progressive increase in SO_4^{2-} suggested that, subsequently, the big driver of chemical weathering at the glacier bed was sulphide oxidation. The consequential increase in both Ca^{2+} and HCO_3^- as SO_4^{2-} increased suggested that sulphide oxidation was primarily linked to carbonate dissolution, giving rise to molar Ca^{2+}:HCO_3^-:SO_4^{2-} ratios of 2:2:1, or 2:1:1 in equivalents (equation 5.1) .

$$4FeS_2\,(s) + 16CaCO_3\,(s) + 15O_2\,(aq) + 14H_2O\,(l) \leftrightarrow 16Ca^{2+}\,(aq) + 8SO_4^{2-}\,(aq) + + 16HCO_3^-\,(aq) + 4Fe(OH)_3\,(s) \quad (5.1)$$

The linear portion of the Ca^{2+} *versus* SO_4^{2-} and HCO_3^- *versus* SO_4^{2-} scatter plots, when SO_4^{2-} > ~50 μeq L^{-1}, is driven by this reaction, and the curvilinear section prior to this, when SO_4^{2-} < 50 μeq L^{-1}, is a function of carbonate hydrolysis initially being the faster reaction, but slowing down as it approaches saturation and sulphide oxidation is starting to occur. That the real molar ratio of Ca^{2+}:HCO_3^-:SO_4^{2-} was ~1.7:1.5:1 suggested that ~75 % of the protons derived from sulphide oxidation were used to dissolve carbonates and ~25 % to dissolve silicates. Glaciers really are very good at dissolving the trace carbonate component of the bedrock. The global geochemical weathering ratio of carbonates:silicates is 1.3:1 (Holland, 1978), but at HGA it is ~3:1.

The relatively simple-minded subglacial chemical weathering model I had developed at Gornergletscher (Tranter *et al.*, 1993) seemed to be working in concept, but was found wanting by the fact that some subglacial SO_4^{2-} concentrations were >~400 ueq L^{-1}. Initially, I had thought that the concentration of O_2 in supraglacial meltwaters controlled the amount of sulphide oxidation occurring at the glacier bed, since subglacial sources of O_2 are limited. The O_2 content of supraglacial meltwaters at HGA could dissolve a maximum of ~380 μeq L^{-1} of SO_4^{2-}, assuming the meltwaters were initially in equilibrium with atmospheric O_2 prior to their descent to the bed. The only way to sustain the idea that O_2 limited sulphide oxidation was to invoke special case pleading, such as over-pressuring of O_2 by gas entrapment at the base of moulins. It had been drilled into me, both at UEA and Southampton, that special case pleading was a smoke screen masking a bad hypothesis. I had to dream up a better hypothesis.

I thought of the early marine sedimentary diagenesis that I so loved learning and teaching (Berner, 1980), and felt that other oxidising agents, such as NO_3^-, Mn(IV) and Fe(III), were likely to be the things that were oxidising the sulphide after the O_2 was used up. This meant that the subglacial waters and sediments were anoxic, and suddenly opened up a whole set of other geochemical reactions in my imagination. I knew that sulphide oxidation was usually microbially catalysed, since microbes make a living by catalysing reactions between different redox pairs, but we had thought previously that the seemingly hostile bed of the glacier, being cold and dark, and flushed by flowing water, would be devoid of microbial life. I painfully remembered John Parkes, a prominent geo-microbiologist in Earth Sciences at Bristol, telling me in a seminar I gave when I first arrived at Bristol that sulphide oxidation under glaciers must be microbially mediated because abiotic sulphide oxidation is so slow. Further, Gerry Jones, a snow chemist from Quebec and always well ahead of the game with his vivid and colourful imagination, told me that he had reviewed the second Arolla project grant application and had questioned whether glacier beds were truly abiotic. Perhaps there really was microbial life at glacier beds after all.

Using the borehole water level data, Bryn Hubbard had identified a zone between the channelised and distributed drainage systems termed the channel marginal zone (Hubbard *et al*., 1995), and the chemical weathering reactions in this zone required a subglacial source of CO_2 (Tranter *et al*., 2002). In other Earth Surface environments, CO_2 is usually generated from the oxidation of organic matter (Drever, 1997), and this oxidation almost always involves biological activity (Berner *et al*., 1993). I chatted this over with Martin and we both felt that there must be microbial life beneath glaciers. John Parkes told us that this was easy to establish. He simply needed some subglacial water samples that should be transferred into a sterile fixing solution immediately after sampling. I am not proud of what happened next (see Text Box 5.1), but the outcome was a paradigm shift in our understanding of glacial chemical weathering.

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Text Box 5.1 – Heathrow airport and illegally shipping formaldehyde by plane (please don't try to do this; I've never done anything like this since)

John Parkes suggested that we collect some borehole water and sediment samples for him and Barry Craggs to examine, with a view to counting any microbial cells present. He gave me a small box of 250 mL sterilised bottles containing formaldehyde. I packed them in my hard suitcase, along with my yellow ice axe (a great colour for me, I am terrified of heights, particularly on glaciers and near moulins) and turquoise crampons. I set off for Heathrow *en route* to Arolla, got stuck in traffic and arrived in the Geneva check in queue very late. I was called from the queue-in and asked to hand carry my luggage through security and onto the plane. The black comedy started when security called me to one side, escorted me into a side room and two armed guards asked me to open my suitcase. The guards asked me what I was carrying and for what purpose, and I explained that I was a glaciologist going to the Swiss Alps to collect some water samples for microbiological analysis. The guards asked me to take out the ice axe and to unwrap the crampons, which I did. So far so good, but I was very nervous about the formaldehyde. They asked me what the bottles were for, and what the liquid was. I said that the bottles were specially cleaned and sterile, and that the liquid was a preservative for the microbes I hoped to sample. They asked whether it was flammable, and I said categorically "no", because at that moment I honestly thought that formaldehyde was inflammable. They asked me to open a bottle and I said I would, but that it would harm their nostrils if they inhaled it. They were happy with the bottles, but not very happy with the ice axe and

crampons. I had to give them to the guards, who escorted me to the plane. The flight was waiting on me, and all the luggage was taken and stored. I sat down and then thought about formaldehyde. It was flammable…… The plane taxied to take off, and I started to worry about whether or not the bottle tops were tightened properly. I thought I could smell organic solvent as the plane took off and was horrified. I could see babies and small children in the plane, and I thought I was poisoning them. It took me about 30 minutes to calm down and listen to the sensible voice in my head, which said that all was well and that I was imagining everything. The good thing to come from this action of some stupidity and irresponsibility is that I haven't tried to pull a stunt like that since.

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5.3 A Game Changer – Microbes Found at Glacier Beds

We sampled the concentrated, turbid meltwaters rising up from the base of boreholes as the discharge from Haut Glacier d'Arolla increased. We returned them to Bristol, where Barry Craggs stained the samples with acridine orange. He found plenty of microbial cells attached to the suspended sediment. Many of the cells were dividing, indicative of them being alive and active in the subglacial environment. Microbes usually like to be attached to particulates, and there were more microbes in the more turbid samples (Fig. 5.7). The results caused something of a stir when we published the work (Sharp *et al*., 1999). The wet beds of alpine glacier beds could now be thought of as habitats for microbial life. Questions revolved around what types of microorganisms were there and what were they doing, and whether our results could be scaled to other ice masses.

Martin got all this much more quickly than I did. I figured it made sense that wherever there was water, there was life, but Martin appreciated the paradigm shift for the discipline better than I did to start with. John Parkes did not need any convincing that microbes could live under glaciers. His research into the deep, cold biosphere of marine sediments threw up many parallels with glacial systems (Parkes *et al*., 2005). First, pressure and temperature were not problems – microbes live in the cold waters in oceanic trenches, where water depths can be over 7 km. The paucity of fresh organic matter wasn't necessarily an issue, because these trench sediments are organic carbon poor too. Finally, glacier erosion introduces a fresh and continual supply of crushed sulphide minerals into the subglacial environment, and mid-ocean ridge biological communities could flourish on sulphides, albeit in waters warmed by geothermal activity and in larger quantities. We could not think of a reason for our results to suggest anything other than that microbes colonised alpine glacier beds, and that certain glaciological processes, including the production and/or delivery of water to the bed and

glacier erosion, provided the microbes with suitable habitats and energy sources. We had produced a paradigm shift for our discipline.

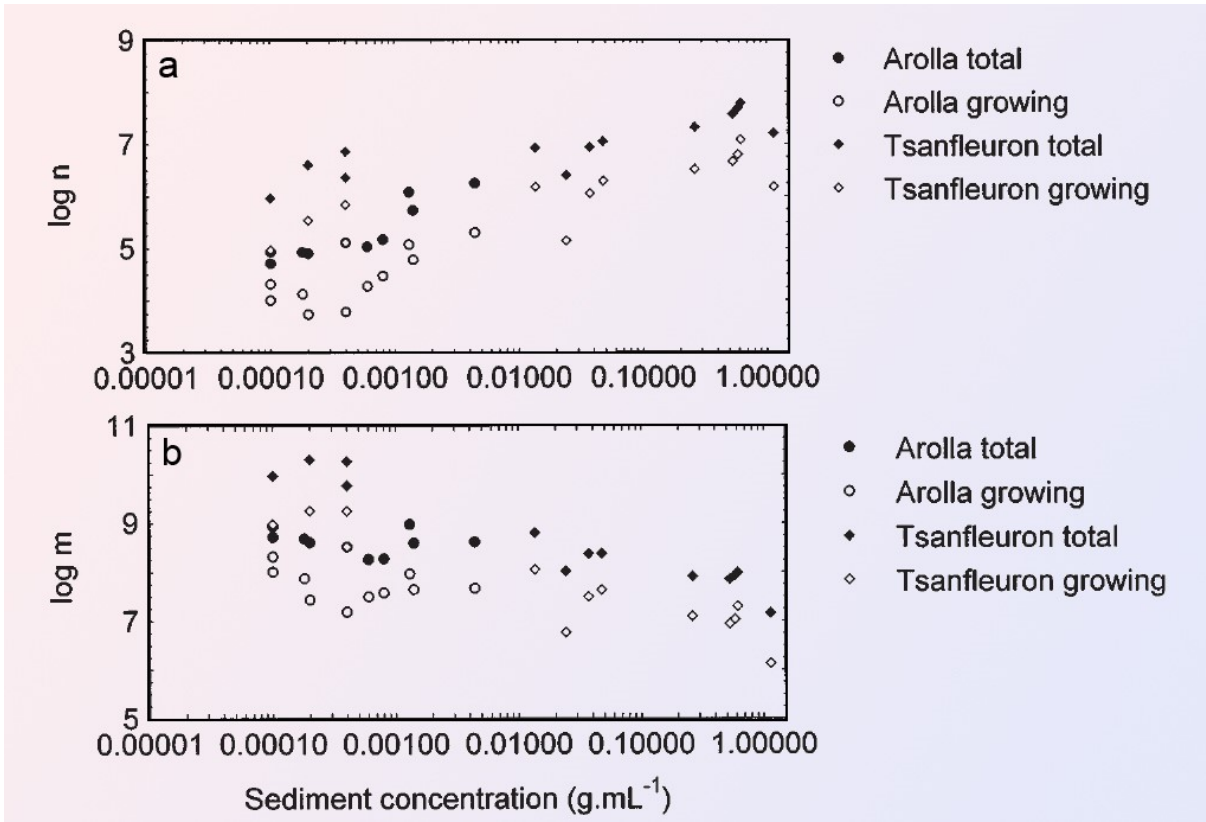

Figure 5.7 The association of microbial cell numbers and suspended sediment concentration (grams per mL) in meltwater from the base of boreholes at Haut Glacier d'Arolla and basal ice from Glacier de Tsanfleuron (modified from Sharp *et al*., 1999).

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6. BIGGER COLDER ICE MASSES

6.1 The England Effect (MS)

By 1989, I was starting to think about how to use my first period of sabbatical leave. In those days, I spent a lot of time with the Quaternary Geologists in Cambridge, and ate lunch regularly with Phil Gibbard, Richard Preece, and Rainer Grün. That year, we had a sabbatical visitor from Canada, John England from the University of Alberta, who had spent his entire career trying to work out the history of Quaternary glaciation and sea level change in the Canadian Arctic Archipelago. John joined us for lunch from time to time and we hit it off right away. He had a crazy sense of humour and persuaded me to consider spending my sabbatical in Edmonton, with the carrot that he would take me to do fieldwork on Ellesmere Island if I did.

As it happened, I had been starting to think about how little we knew about the hydrology of glaciers in environments that were much colder and drier than the Alps, and about where would be a good place to study this. I had considered Svalbard, which was starting to attract a lot of attention at the time, and ruled it out because I thought the climate there was too maritime to produce big differences from what we were seeing in temperate environments. Ellesmere Island had a much colder, drier, and more continental climate, and seemed like a good alternative, so I decided to take John's offer and my family and I headed to Edmonton for the sabbatical in January 1991. John and I went up to Ellesmere Island in July (with the added carrot of a trip to Skaare Fjord on Axel Heiberg Island at the end of the Ellesmere fieldwork). Here I joined my Ph.D. student Bryn Hubbard and future Ph.D. student, Dave Burgess, who were studying basal ice and thrust block moraines formed by the polythermal glaciers there.

On Ellesmere Island we worked mainly on raised glaciomarine sediments along the west side of Nares Strait. There were tantalising glimpses of the glaciers in northwest Greenland but we saw little of the Ellesmere Glaciers until our flight out to Eureka at the end of the season, when we flew over the Agassiz ice cap. I was struck by the number of large lakes on the surface of these glaciers, some of which were drained by very impressive supraglacial meltwater channels. Others, however, showed evidence of having frozen over at the end of the previous melt season and then drained *in situ* from beneath the resulting ice cover, which was left sitting on the floors of the lake basins, having fractured into very large chunks. This was very different from anything I'd seen in Iceland, Alaska, Norway, or the Alps, so it seemed like there was a story to pursue.

6.2 A Move to Canada and an Arctic Focus

The end shot of all this was that I moved to the University of Alberta in 1993, and set about building a research programme to study the hydrology and dynamics of glaciers on Ellesmere Island. I continued to work at Arolla until 1997, which meant some very busy summers. I was fortunate to be able to bring two graduate students from the UK with me to Canada to undertake Master's programmes. Mark Skidmore and John Woodward have both, respectively, gone on to make substantial contributions to glacier hydrochemistry/microbiology and glaciology. I was also fortunate that the very first class I taught in Canada (Field and Lab methods in Physical Geography) introduced me to two very bright undergraduates, Anthony Arendt and Joel Barker, who were both keen to work on glaciers as well.

My main goal for the first year in Canada was to find a large (but not too large) Arctic glacier that showed evidence of both surface drainage entering the glacier and proglacial outflow. Given the climate in the Canadian Arctic Islands, I anticipated that any such glacier would have a polythermal temperature regime and thus differ significantly in terms of its hydrology from Haut Glacier d'Arolla. Mark went to work on examining aerial photographs and we eventually identified John Evans Glacier (Fig. 6.1), on the east coast of Ellesmere Island, as a target that seemed to meet our criteria and that looked reasonably accessible and workable.

Figure 6.1 John Evans Glacier, Ellesmere Island.

Mark, John, Anthony and Joel made up the field team for our first season on Ellesmere Island. Mark and Joel were interested in glacier hydrology, while Anthony and John were more interested in ice-climate interactions. We went to the glacier for the first time in May 1994 and the field crew was in place until August. It turned out that the glacier was exactly what we had been looking for, although, at 160 km^2, it was much bigger than anything we had worked on previously. It was a challenge to explore the entire glacier on foot, especially during the "slush season", when the snowpack was being removed from the glacier by melting. The runoff volume generated by a glacier this size made it an even bigger challenge to monitor from a hydrological perspective. We did eventually find a way to work there using a combination of judiciously placed camp sites, skidoos for travel in spring, when equipment could most easily be moved around and deployed, and a lot of hiking in summer. In the first season, there was

an additional challenge since Mark had injured his knee in a skiing accident the week before departing for the field. This left him pretty immobile and not really able to walk, so arrangements were made, for the period while there was still snow cover, to tow him on a sled from the campsite to the streambank nearest to the water sampling site from where he could give instructions as to where, what, and when to sample. He then had to be pulled back to camp every evening!

We worked at John Evans Glacier until 2001. During that time, Luke Copland, Sarah Boon, Maya Bhatia, Trudy Wohlleben, Pete Nienow and Rob Bingham also worked on the project. We did our best to study the system in the same way that we had studied Haut Glacier d'Arolla, but we could never afford to drill at John Evans Glacier. Sadly, 23 years on, that situation has not changed for Canada-based researchers and there has yet to be a hydrologically-motivated hot-water drilling project in the Canadian High Arctic.

In the first field season at John Evans Glacier, we discovered that the supraglacial streams which annually re-occupied major channels incised into the surface of the upper glacier eventually drained into the glacier *via* a crevasse field located about 4 km upstream from its terminus (Fig. 6.2). Early in the melt season, waters draining into these crevasses seemed to drain relatively slowly towards the terminus, suggesting there was some form of subglacial water storage prior to the onset of outflow at the terminus. Once outflow started, which was usually about three weeks after melt onset, and 5 days after water started to drain into the glacier, water exited the glacier by three different pathways that were activated sequentially. First, an artesian fountain up to 3 m high emerged on the glacier surface about 200 m upstream from the terminus (Fig. 6.3). More or less synchronously, water began to upwell through subglacial sediments over an area about 30 m wide in front of the glacier terminus. Finally, up to a few days later, channelised flow emerged at the glacier-bed interface in a different location to the initial upwelling. In subsequent years, we discovered that the number of outflow channels varied from year-to-year, and that the channelised outflow tended to start a few days later than the artesian flow and upwelling. The precise locations of outflow also varied a bit between years. The chemistry of the initial outburst waters was, however, very similar at all three locations – dominated by Ca^{2+} and SO_4^{2-} - suggesting a common source and/or transport pathway for all subglacial waters (Skidmore and Sharp, 1999).

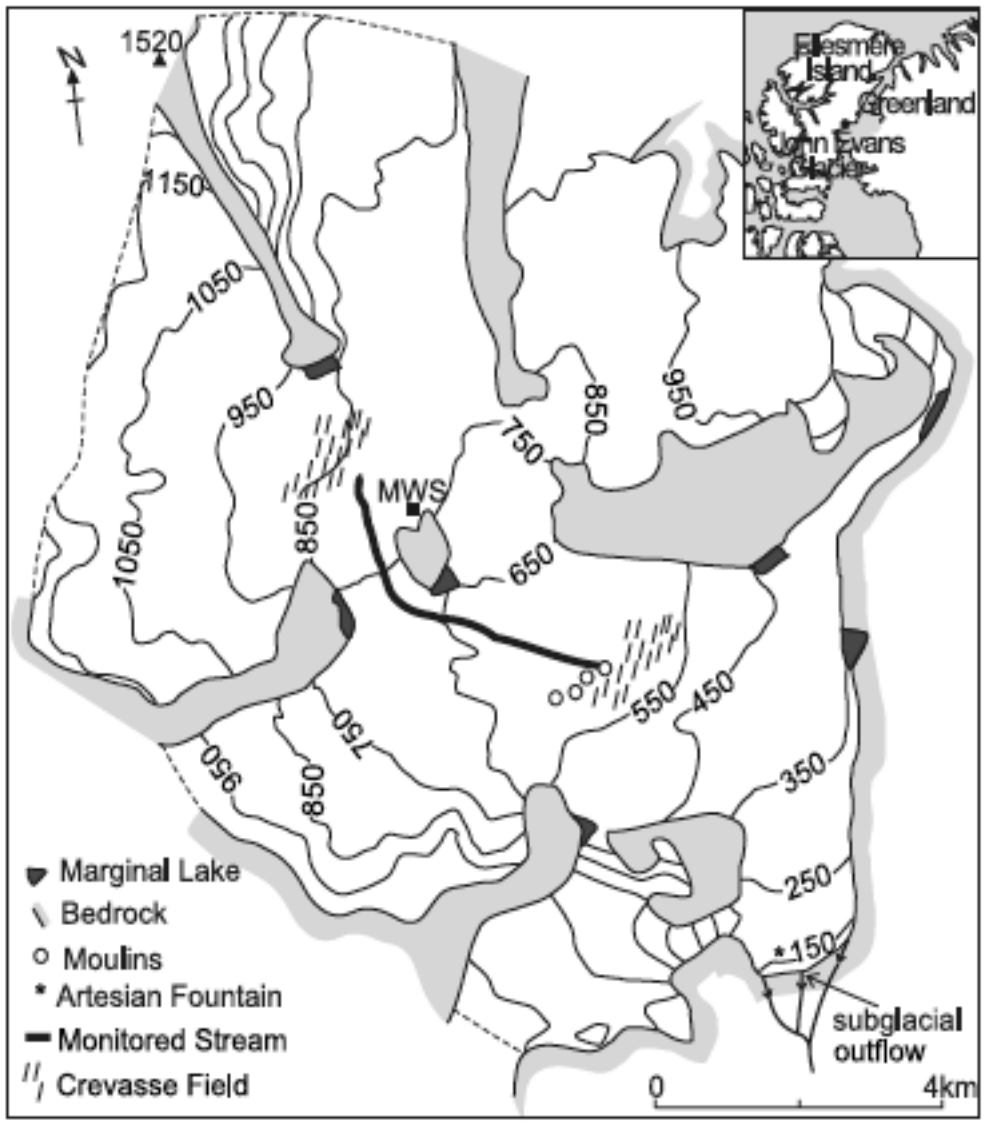

Figure 6.2 Location of John Evans Glacier (Inset) and of the crevasses/moulins (open circles) where surface streams drained into the glacier after an initial period of surface ponding, and the artesian fountain (asterisk) and subglacial outflow where they emerged near the glacier terminus (from Boon and Sharp, 2003).

Figure 6.3 Artesian fountain, John Evans Glacier, Ellesmere Island.

Runoff hydrograph shapes, discharge volumes, and the temporal separation of discharge events varied somewhat between years. Some hydrographs were positively skewed like the "sudden break" outburst events that have been linked to water pocket ruptures on Alpine glaciers, although they lasted for days rather than hours. This suggested to us that the initial release of water in each melt season required hydro-fracturing of a thermal dam at the glacier terminus, which was presumably frozen to the bed in winter (when temperatures routinely dropped below -40 °C). Other hydrographs were negatively skewed, suggesting gradual opening of the outflow pathway, most likely by melting of the ice by the frictional heat generated by the water flow, followed by a sudden water outburst that terminated abruptly either as the water supply ran out or was insufficient to prevent creep closure of the drainage pathway. Outflow rates dropped very substantially or even ceased in the periods between outbursts, suggesting that the outlet channels might have closed down after the drainage of the subglacially-stored water. The occurrence of multiple outbursts, however, suggested a repeating cycle of filling and drainage of supraglacial and/or subglacial water reservoirs that was presumably linked to repeated expansion and contraction of the subglacial drainage pathways (Skidmore and Sharp, 1999).

There was some evidence that the sign of the skewness of the outburst hydrographs was linked to the intensity of melt in the period leading up to the outburst (Skidmore and Sharp, 1999). Intense melt tended to promote hydro-fracturing as a means of drainage pathway development, which resulted in positively skewed (rapid rise, slow decline) hydrographs, while less intense melt promoted channel growth by wall melting and resulted in negatively skewed (slow rise, rapid decline) hydrographs. Significantly, there was little or no sign of diurnal variability in the runoff discharge, suggesting that melt-induced variability in runoff production was buffered by significant water storage on and/or within the glacier. Meltwater discharge rates thus seemed to be linked to the volume of water storage in and/or on the glacier rather than directly to the rate of meltwater production. This was essentially the opposite of what we had found at Arolla, where short term variations in melt rates were clearly reflected in the discharge hydrograph.

Larger water storage volumes and/or longer water storage times at the bed of John Evans Glacier both suggested the possibility for more rock-water interaction than at Arolla (and this was likely amplified by the fact that the local bedrock was dominated by soluble carbonates and evaporites, rather than the metamorphic rocks found beneath Haut Glacier d'Arolla). This was confirmed by measurements of the sulphate content and electrical conductivity of the initial outburst waters which were typically on the order of 2000-3000 ueq L^{-1} SO_4^{2-} and 0.05-0.65 S m^{-1} respectively (Skidmore, 1995).

6.3 Linking Surface and Subglacial Hydrology

In the next phase of the work, we tried to link discharge variability at the glacier snout to processes taking place on the glacier surface. This took us a few years because the early part of the melt season on the glacier was characterised by a "slush season", when the entire snowpack became water-saturated and turned to slush. On flat surfaces, this was mainly unpleasant because we were often wading through thigh-deep slush to get around the glacier. On, or immediately below, steeply sloping sections of the glacier, however, it was just plain dangerous because the slush routinely failed and travelled rapidly downglacier as slush flows or slush avalanches that would have been quite capable of wiping out a camp or sweeping away a person. Hence, there was a 2-to-3 week period every year when we were reluctant to spend much time on the glacier surface. Unfortunately, this also meant that we were unable to make direct observations of what was going on in likely one of the most important parts of the hydrological year.

Ultimately, we got around this challenge using time-lapse cameras mounted on nunataks and the valley walls. We discovered that many of the large supraglacial meltwater channels

contained roofed sections, suggesting either that these channels were partially-unroofed, shallow englacial channels, or that deep incision of surface channels allowed roofs to form by ice creep from the channel sides (so-called "cut-and-closure" channels). The roofed sections of the channels were often blocked with snow at the end of winter, and hydrological connectivity between channel sections on either side of the blockages was low in the early melt season. As a result, the unroofed sections tended to fill with water at different rates until the snow that was causing the blockage between adjacent channel sections became water-saturated and failed, allowing head matching between the upstream and downstream sections. This process occurred many times at different locations along a given channel before continuous flow was established each spring.

Sarah and I monitored discharge at the downstream end of a 3 km long section of channel at the point where it intersected a large crevasse on the channel floor (Fig. 6.2). At this location, the ice was 150 m thick. Within three days of the onset of surface meltwater drainage, the crevasse became filled with water, and water began to pond in the stream channel upstream from it (Fig. 6.4a). The water level rose for 11 days, and eventually reached a depth of 6.9 m within a 200 m long pond (Fig. 6.4b). During the period of ponding, the channel-floor crevasses became measurably wider, air bubbles were seen rising from them into the pond, and frequent deep cracking noises were heard. On 8 occasions, short periods of falling water level punctuated the generally rising water level trend, indicating incipient, but not sustained, drainage into the channel-floor crevasses, which appeared to be getting wider and deeper over time. Ultimately, on June 29, the pond drained completely in less than an hour. Once it had emptied, 5 new crevasses, oriented perpendicular to the long axis of the channel, were visible on the channel floor (Fig. 6.4c).

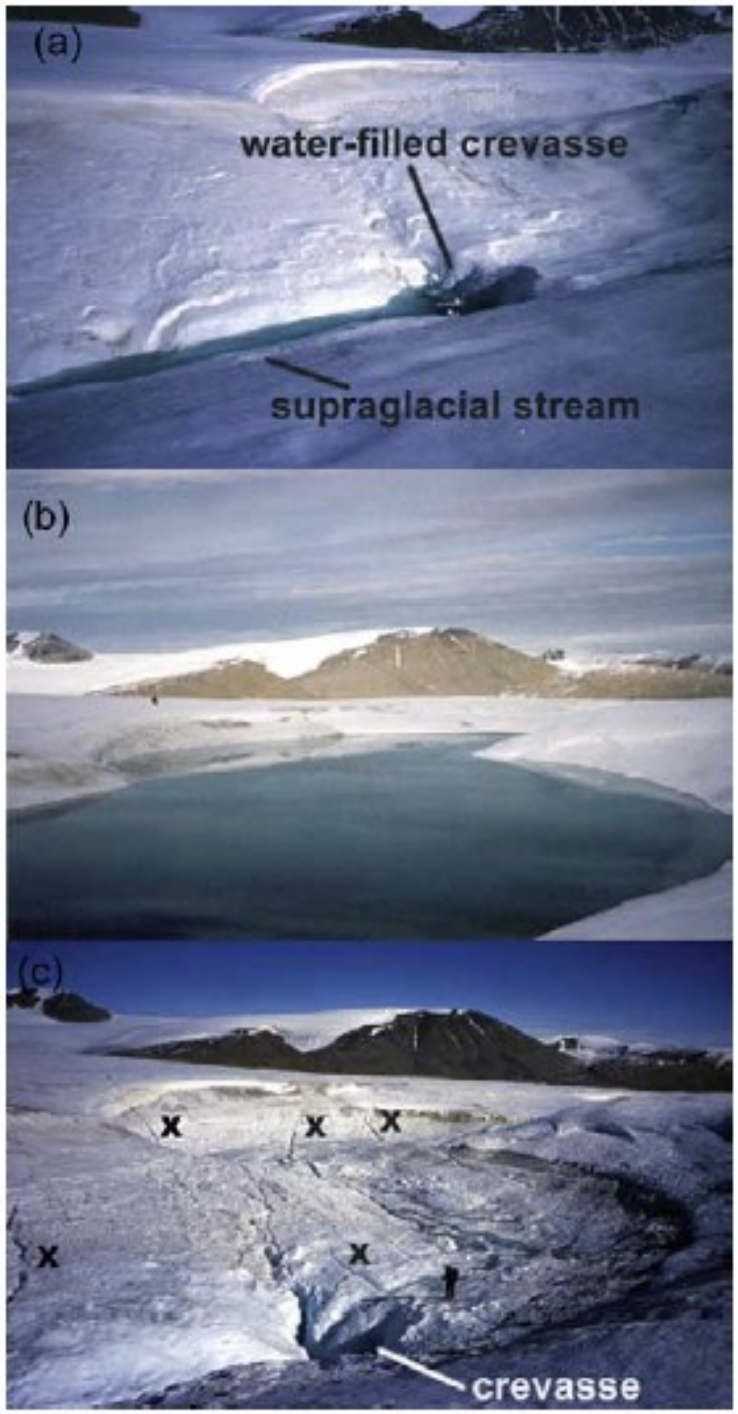

Figure 6.4 Sequence of **(a)** initial ponding of supraglacial meltwater above a crevasse on John Evans Glacier (16 June), **(b)** supraglacial lake formation in the crevassed area (28 June), and **(c)** lake drainage by crevasse hydro-fracture (30 June). Fresh crevasses formed during the period of ponding and drainage are marked with an ‘x‘ (from Boon and Sharp, 2003).

The following day, the usual turbid, solute-rich meltwater began to upwell through sediments at the glacier terminus and the "artesian fountain" appeared on the glacier surface about 200

m above the glacier terminus (Boon and Sharp, 2003). We inferred that this outflow involved the water that had drained abruptly into the glacier the day before. However, if that was the case, the water had become significantly enriched in solute and fine sediment during its transit through the glacier. As Mark had discovered previously, the outflow waters were rich in calcium and sulphate, which suggested rapid dissolution of evaporite minerals, such as gypsum, that are present in the local bedrock. Alternatively, the dilute water that drained into the glacier could have displaced solute-rich water that had spent the preceding winter at the glacier bed.

An essentially identical process of fracture-driven penetration of surface meltwater to the glacier bed had been hypothesised by the Russian glaciologist, Bulat Mavlyudov (Mavlyudov, 1995, 1998), and incorporated schematically by Neil Arnold into one of the first ice sheet models to try to simulate the coupling between glacier hydrology, ice sheet flow, and ice sheet evolution (Arnold and Sharp, 2002). It was exciting for me to see, for the first time, direct evidence in support of Mavlyudov's hypothesis. Subsequently, in 2014, it was a real pleasure for me to have the opportunity to talk to him about how our observations supported his ideas when I quite coincidentally bumped into him on King George Island, Antarctica, where he was in charge of the Russian scientific base. The basic idea, that sudden, fracture-driven drainage of supraglacial lakes through the underlying ice body is a key process for connecting the surface and subglacial drainage systems of large ice masses, has since been reinforced by observations on the Greenland Ice Sheet, and has now become a key component of models of ice sheet hydrology. Essentially the same process has also been shown to play an important role in the sudden break-up of some Antarctic ice shelves.

Through her work, Sarah Boon was able to show, for the first time, that the initiation of runoff at the glacier terminus each year lagged multiple sudden drainage events involving water stored on the glacier surface in the early part of the melt season, in which the ponded surface water drained abruptly into crevasses. Subsequently, Rob Bingham demonstrated that the period in late June and early July, when meltwater runoff was initiated and supraglacial lakes drained, was also characterised by acceleration of glacier flow downstream from the water input location and prior to the occurrence of outburst events at the glacier terminus. His work, and that of Luke Copland, suggested that the flow of the glacier was very sensitive to the timing and spatial pattern of water inputs from the surface (Bingham *et al*., 2003, 2005, 2006; Copland *et al*., 2003a,b).

In his M.Sc. thesis, Mark Skidmore had made a detailed analysis of the major ion chemistry of 7 different streams draining from John Evans Glacier – a supraglacial stream, 3 proglacial streams, one ice marginal stream, the artesian fountain, and the subglacial upwelling

(Skidmore and Sharp, 1999). He found that the chemistry of waters from the supraglacial, proglacial, and ice-marginal streams suggested that calcite dissolution was the main solute source, and that dissolution of atmospheric carbon dioxide in the meltwater to form carbonic acid was the main proton source. By contrast, waters from the artesian fountain and the subglacial upwellings had chemistries consistent with dissolution of gypsum as the major solute source. They also contained more magnesium than expected, suggesting that de-dolomitisation (*i.e*. incongruent dissolution of dolomite that resulted in selective removal of magnesium) might be occurring in the subglacial system. Mark also thought that the chemistry of the fountain and subglacial upwelling waters suggested that subglacial precipitation of calcite was occurring. This was presumably driven by the release of calcium by dissolution of gypsum and dolomite, which continued after the subglacial waters became saturated with respect to calcite and caused them to become supersaturated with respect to that mineral.

Mark also found that significant weathering was occurring in the proglacial area when dilute waters draining off the glacier surface first made contact with proglacial sediments. In short, despite obvious differences in both the bedrock geology and the physical hydrology of the glaciers, there were many similarities between the processes by which meltwaters acquired solute at John Evans Glacier and at Arolla. Solute acquisition was dominated by dissolution of the most reactive mineral phase available, which was calcite in both cases. The differences in meltwater chemistry between the two sites were largely due to their geological differences – specifically the presence of gypsum and dolomite, and the absence of sulphide minerals such as pyrite, in the bedrock at John Evans Glacier. At neither location did dissolution of silicate minerals appear to be a major solute source.

6.4 Microbial Involvement in Arctic Subglacial Weathering

After completing his M.Sc, Mark decided to stay in Alberta for his Ph.D. and to conduct research into the role of microbes in the chemical weathering processes that he had documented in his M.Sc. thesis (Skidmore, 1995). In this, he was somewhat guided by the speculation about how microbes might be involved in subglacial weathering that we had included in the *Geology* paper (Sharp *et al*., 1999) in which we had first reported the occurrence of microbes in subglacial meltwaters from Haut Glacier d'Arolla and basal ice from Glacier de Tsanfleuron in Switzerland. This speculation focused on how microbes might obtain energy in what we presumed to be a light-free subglacial setting. Mark decided to investigate whether microbes were also present in the relatively cold glaciers of Ellesmere Island and, if they were, to conduct experiments to test hypotheses about how they obtained their energy.

To facilitate this work, we began a rewarding and productive collaboration with University of Alberta microbiologist Julia Foght.

Before discussing Mark's work in more detail, it is worth outlining the discussion that we had presented in the *Geology* paper regarding the suitability of glacier beds as microbial habitats. First, these environments are overlain by an insulating layer of glacier ice and are thus protected from the extreme temperatures that can occur on the glacier surface. Second, if the ice temperature reaches the pressure melting point at, or immediately above, the glacier bed, there will be water at the bed. This water acts as a source of nutrients, dissolved gases, and fine particulate material (both organic and inorganic). Thus, it may itself be a viable microbial habitat, regardless of how it is distributed across the glacier bed or within the basal ice.

Potential nutrient sources in the subglacial environment include (i) surface-derived meltwaters that reach the glacier bed, bringing species such as nitrate and ammonium that can be leached from supraglacial snow, (ii) subglacial meltwaters, a potential source of limiting nutrients such as Fe and Si, that would be derived from rock weathering, and (iii) sulphide oxidation that would be a possible source of colloidal Fe, and of sulphate, which is a terminal electron acceptor. Glacially-overridden soils, sediments, and plant material could be a source of organic carbon, a potential substrate for heterotrophic microbial respiration. Thawing of permafrost overridden by glaciers and ice sheets might be a source of microbes (which were thought to mediate many rock weathering reactions) to the subglacial environment, as might the flow of ice and/or meltwater that could transport microbes to the glacier bed from the glacier's surface and/or margins.

We thought that microbially-mediated oxidation of organic carbon and/or sulphides were likely the main sources of protons at glacier beds. Demonstrating the occurrence of the former would potentially overturn previous arguments that the lack of a subglacial CO_2 source would limit the global importance of subglacial chemical weathering. In support of this idea we pointed out that about 25 % of the world's soil organic carbon pool (an amount of C equivalent to more than 50 % of the amount now found in the atmosphere) is currently found in areas that were covered in glacier ice during the last glaciation. If this were also the case during the last interglacial, then much of that interglacial carbon might have been overridden by, and sequestered beneath, the last great ice sheets, where it would have provided a substrate for microbial respiration. Interestingly, Roland Souchez and co-workers (Souchez *et al*., 1995) had published gas content analyses from debris-rich basal ice in the GRIP ice core from Greenland that showed very high concentrations of both carbon dioxide and methane in that ice (Fig. 6.5). This encouraged us to pursue the idea that subglacial biogeochemistry might

turn out to have some global significance. Mark's Ph.D. was a first attempt to evaluate the viability of that hypothesis.

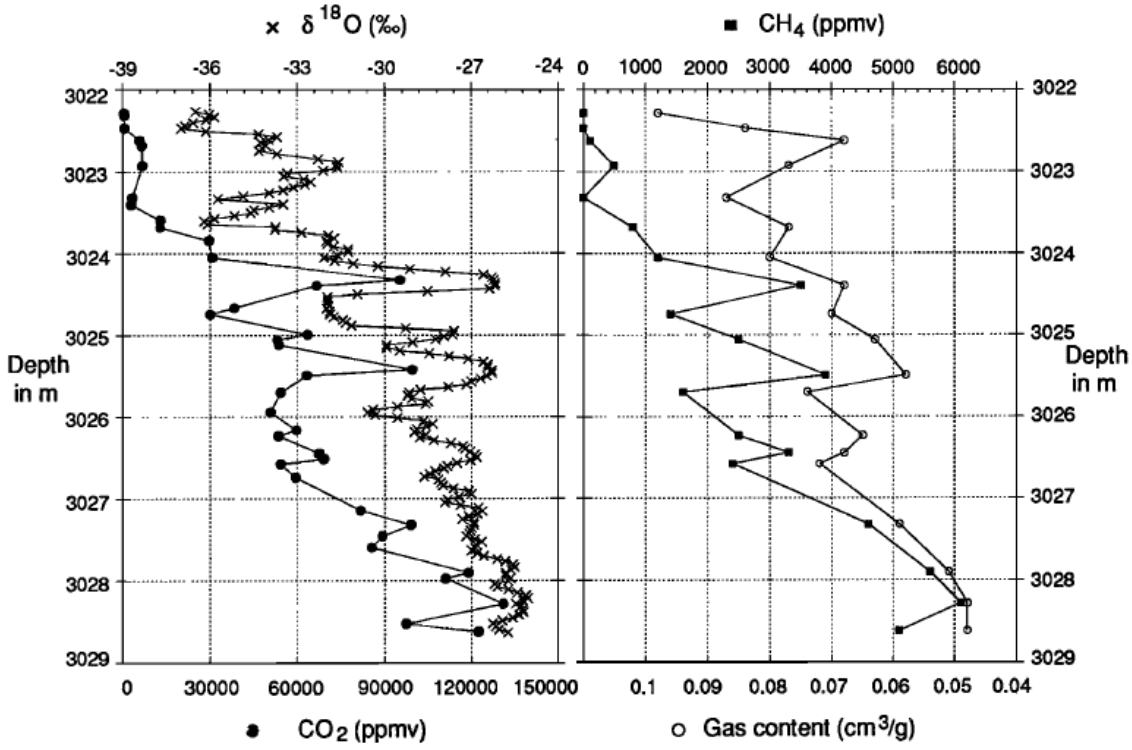

Figure 6.5 CO_2, CH_4, delta^{18}O and total gas content in the basal silty ice from the GRIP ice core, Greenland (modified from Souchez *et al.*, 1995).

For his first set of experiments, Mark collected (aseptically) a series of 4 litre subglacial and supraglacial meltwater samples from John Evans Glacier in 1996. These samples had different chemical compositions and suspended sediment concentrations, and were used to determine whether or not microbes were present in the environments from which they were collected. Each sample was amended in the field with 10X sterile R2A growth medium to a final concentration of 1/10 strength R2A. On return to the lab (after storage on ice) these samples were incubated stationary in the dark at <4 °C. After 7 weeks of incubation, the subglacial sample had greatly depleted dissolved oxygen content (1.7 ppm *vs* initial 10.9 ppm O_2) and lower pH (6.5 *vs* 7.8) than at the start of incubation, and it contained 0.7 ppm of hydrogen sulphide, which was not detectable in the initial sample. The amended supraglacial sample showed no such chemical change.

Within six weeks, incubations of samples containing either anaerobic nitrate or sulphate medium turned the samples either brown (nitrate) or black (sulphate) and turbid, while incubations of unamended water (either subglacial or supraglacial) showed no or minimal changes. Since bottles inoculated only with the lab control medium remained sterile, the

medium was clearly not the source of the anaerobic organisms that produced the changes in the other inoculations. These initial experiments therefore documented the presence of viable, respiring anaerobic microorganisms in subglacial waters, and suggested that they were capable of reducing both nitrate and sulphate (Skidmore *et al*., 2000).

Mark also carried out aerobic plating experiments using unamended subglacial waters and these yielded $>10^3$ colony forming units (CFU) m/l of water (pigmented yellow or orange), compared with only 10^2 CFU for incubations at 22 °C. Colonies taken from the 4 °C plates did not thrive at 22 °C, suggesting they were composed of true psychrophiles, while colonies from the 22 °C plates did also grow at 4 °C, indicating that they had wider thermal tolerance. Cultures of subglacial waters amended with R2A always produced $>10^6$ CFU m L^{-1}, regardless of incubation temperature, and the organisms that formed these colonies were normally non-pigmented. The unamended supraglacial water sample produced 10^3 CFU mL^{-1} on plates at 4 ˚C, most of which were pigmented, but only 10 % as many at 22 ˚C. The lab medium control yielded no colonies after 3 months at either incubation temperature, indicating that the microbes cultured were derived from the subglacial water samples. An interesting question is whether (as seems likely) the presence of pigmented organisms in the supraglacial samples and their absence from the subglacial samples is a reflection of the difference in degree of exposure to UV radiation between the supraglacial and subglacial environments.

To check the sterility of the amendment process, Mark incubated a laboratory control of 3 litres of heat-sterilised distilled water for 2 months at 4 °C. After the 2 months, two 100 mL samples of the control were filtered through 0.2 um filters to capture viable microbes, and then incubated for 2 months at either 22 °C or 4 °C to culture any recovered microbes. However, neither culture produced microbial colonies, indicating the sterility of the amendment.

After these incubations, Mark inoculated subsamples into 50 mL of either pre-chilled, quarter strength, nitrate or sulphate medium that had been pre-gassed with sterile 10 % CO_2/balance N_2, and incubated stationary in the dark at 4 °C. Over time, the nitrate medium became browner and more turbid than parallel uninoculated media, while the sulphate medium became blacker due to sulphide precipitation. This work demonstrated that meltwaters from John Evans Glacier contained viable microbes, including aerobic heterotrophs and nitrate and sulphate reducers, and showed that these microbes were active under near *in situ* conditions.

To extend this work further, Mark collected samples of glacier ice and basal (debris-bearing) ice from John Evans Glacier in 1997, and used these for additional incubation experiments. He was able to detect both aerobic and anaerobic microbial activity in samples of basal ice incubated at either 8 °C or 4 °C if the sample was amended with low levels of organic carbon (growth medium), or with a terminal electron acceptor such as nitrate or sulphate. This was

not possible, however, with samples of glacier ice – a result that confirmed the efficacy of the aseptic technique used for sample handling. An important result was that both carbon dioxide and methane were produced in anaerobic cultures of thawed basal ice amended with dilute R2A medium. Concentrations of these gases in the sample headspace were, respectively, 10 and 10^4 times greater than were produced by incubations of thawed glacier ice or uninoculated medium. The $\delta^{13}C\text{-}CH_4$ of the thawed basal ice (-73.3 per mille) indicated a microbial origin for the methane. Incubations of poisoned controls failed to produce depletion of either nitrate or sulphate, and did not produce either carbon dioxide or methane. This experiment demonstrated the presence in the basal ice of anaerobic nitrate and sulphate reducers (Fig. 6.6) and methanogens, and showed that they were active in culture at 4 °C. A separate incubation using thawed basal ice amended with ^{14}C-labeled acetate produced a significant quantity of $^{14}CO_2$, while similar incubations of amended thawed glacier ice and uninoculated control did not. This was further evidence that microbial activity (in this case involving aerobic chemoheterotrophs) was linked to the presence of sediment in basal ice.

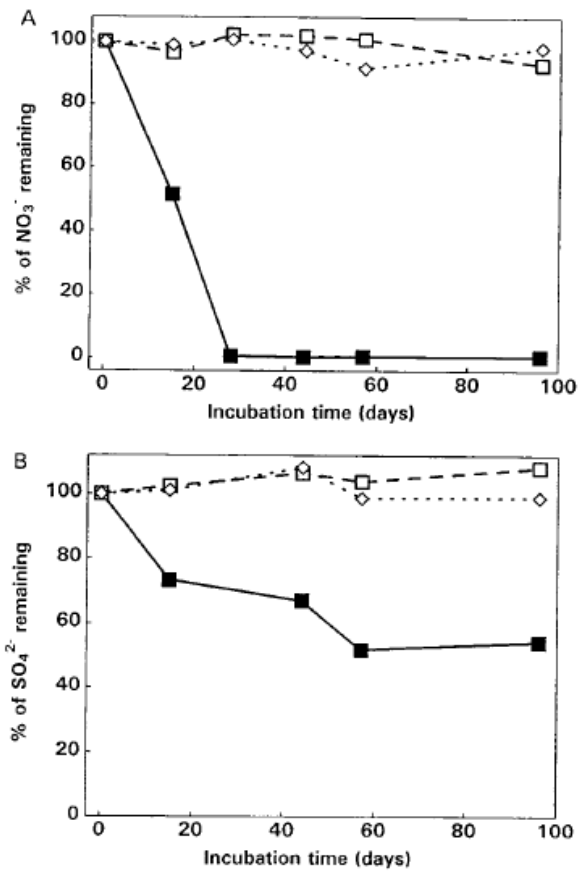

Figure 6.6 Anaerobic incubation of thawed ice samples at 4 °C in the dark. Samples were amended with dilute nitrate medium, (5mM nitrate) **(a)** or dilute sulfate medium (14 mM

sulphate) **(b)**. Symbols: filled square: basal ice, open square: glacier ice, diamond: uninoculated medium (modified from Skidmore *et al*., 2000).

Mark recognised, however, that a major weakness of these initial incubation studies was that they were conducted at temperatures well above the pressure melting point of ice and were thus not truly representative of conditions at the glacier bed. He therefore collected another set of samples in 1998, which he planned to incubate at temperatures as close as possible to the pressure melting point of ice (0.3 °C), and with minimal organic carbon amendment, with a view to trying to detect the occurrence of respiration under near in-situ conditions. In these experiments, he assessed the occurrence of microbial activity by quantifying the aerobic mineralisation of ^{14}C-labeled acetate to $^{14}CO_2$. Separate experiments were performed at –4.8, -1.8 and +0.3 °C, but $^{14}CO_2$ was only produced when the samples were wholly in liquid form. It was, however, produced from unamended, thawed samples of both basal and (to a lesser extent) glacier ice. Amendment with 0.1X R2A medium increased acetate mineralisation in the glacier ice sample and, to a much lesser extent the basal ice sample. This suggested a higher degree of nutrient limitation of microbial activity in the glacier ice sample. Microscopic (Transmission Electron Microscopy) studies of freshly thawed and cultured samples of basal ice revealed prokaryotic cells, including cells undergoing division. Cells were usually observed singly rather than in biofilms or microcolonies (Fig. 6.7).

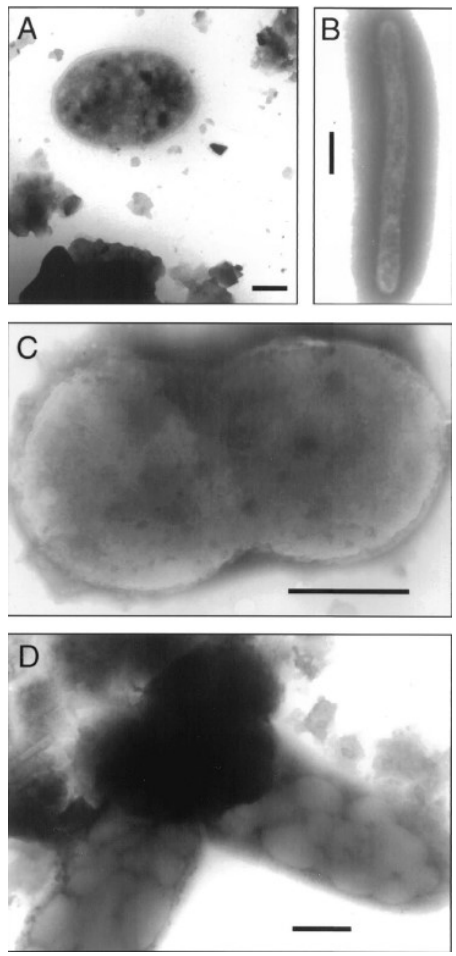

Figure 6.7 TEM images of bacteria in meltwater from basal ice samples. Scale bars = 0.5 microns. **(a)** Coccus associated with sediment from uncultured basal ice immediately after thawing. **(b and c)** Long thin rod (b) and actively dividing cocci (c) from an aerobic stationary culture incubated at 0.3 °C without R2A medium. **(d)** Short, fat rods with inclusions, associated with sediment from an aerobic culture incubated at 4 °C without R2A medium (from Skidmore *et al*., 2000).

Both glacier ice and, especially, basal ice samples contained dissolved and particulate organic carbon, while sediments collected from ice marginal and proglacial locations all contained cyanobacterial mats, mosses, and vascular plant remains. This suggested that glacial overriding of such sediments was a likely mechanism for making allochthonous organic carbon available as a source of energy and carbon for subglacial microbes. Mark thought that glacial overriding might also be an important process for seeding subglacial microbial populations. In addition, he argued that, with localised oxygen input from the melting of basal ice or downward percolation of surface-derived waters, both aerobic and anaerobic microbial activity would be possible at glacier beds, the balance depending upon local circumstances. This could

generate either CO_2 or CH_4, depending on local circumstances, and would be a plausible way to at least partly explain the origin of the high concentrations of these gases observed in the basal ice from the Dye 3 and GRIP ice cores from Greenland (CO_2 40,000 ppmv at Dye 3 and 130,000 ppmv at GRIP; CH_4 6000 ppmv at GRIP). Mark argued, on the basis of a simple calculation, that aerobic respiration of organic carbon, constrained by the supply of O_2 to ice sheet beds by basal melting alone, might convert as much 8.1 Pg of carbon to CO_2 over a glacial cycle. This estimate might be on the low side because it ignored the input of O_2 to glacier beds by surface-derived meltwaters, as well as any potential contribution from anaerobic decomposition of organic carbon. Mark's work effectively established the basis for considering that large ice sheets could be active participants in global biogeochemical cycles, at least on timescales of 10^5 to 10^6 years.

Whilst all this was going on, Julia Foght went on sabbatical to Landcare Research in Hamilton, New Zealand, where she planned to work with Jackie Aislabie who had previously worked on the microbiology of soils in the Dry Valleys of Antarctica. However, this visit also resulted in a collaboration with my first Ph.D. student, Wendy Lawson, who was then working in the Department of Geography at the University of Canterbury in Christchurch. They investigated the microbes found in glacier ice and subglacial sediments at the iconic Fox and Franz Josef Glaciers in New Zealand's Southern Alps – a very wet environment that was a major contrast to the aridity of Ellesmere Island. Here they found concentrations of microbes on the order of 2-7 x 10^6 cells g^{-1} dry weight sediment, and 6-9 x 10^5 colony-forming units g^{-1} dry weight sediment of culturable aerobic heterotrophs. Concentrations of these microorganisms in subglacial sediments were 3-4 orders of magnitude higher than those in glacier ice, and the sediments contained both nitrate-reducing and ferric iron-reducing bacteria, while the glacier ice did not. Nitrogen-fixing bacteria were also found in the Fox Glacier sediment. 37 pure cultures of aerobic heterotrophs at 4 ˚C yielded 23 distinct groups of micro-organisms when analysed using restriction fragment methods applied to 16S rDNA. 11 of these were identified as β-Proteobacteria and phylogenetic analysis showed that they clustered with bacteria such as *Polaromonas vacuolata* and *Rhodoferax antarcticus,* or with clones from permanently cold environments. Sediment samples demonstrated aerobic mineralisation of ^{14}C acetate at 8 ℃, indicating the presence in the subglacial sediments of both viable psychrotolerant microbes and sufficient nutrients to support metabolism. It was beginning to look as though the existence of subglacial microbes might prove to be the norm, rather than the exception to the rule, and that these organisms might represent a globally important reservoir of biological activity that could play a significant role in biogeochemical cycling (Foght *et al*., 2004).

6.5 Provenance of Subglacial Microbes

Maya Bhatia obtained her undergraduate degree in Biology from Queen's University in Ontario and came to Alberta to work with Julia and I for a Master's degree on glacier microbiology. We devised a project for her on John Evans Glacier where she would make a comparison of the composition of the microbial communities found on the glacier surface, at the glacier bed, and in proglacial sediments beyond the glacier margin. The basic idea was to try to determine whether the subglacial microbial community had a unique composition that might reflect adaptation to a unique subglacial environment, or whether it was a simply a mixture of organisms derived from one or both of the two proximal environments that might reasonably be expected to contribute organisms to it. To do this, she collected, and analysed samples of water, ice and sediment from each of the supraglacial, subglacial, and proglacial environments. Maya turned out to be another exceptional student.

Maya used the method of Terminal Restriction Fragment Length Polymorphism (TRFLP) to analyse the bacterial 16S rRNA genes that were amplified from samples obtained from the full range of sub-environments. Her goal was to determine whether the microbial communities found in each sub-environment could be differentiated from each other. Her main finding was that the communities obtained from subglacial water, basal ice, and subglacial sediment were distinctly different from those found in supraglacial meltwater and in proglacial sediments (Bhatia *et al*., 2006). She identified 142 unique terminal restriction fragments (T-RFs), 60 of which occurred only in subglacial samples, 12 only in supraglacial samples, and 23 only in proglacial samples. Only eight T-RFs were found in all three sets of samples. The subglacial samples shared 20 T-RFs with the supraglacial environment and 16 with the proglacial environment, so the majority (63 %) of the T-RFs found in the subglacial environment were only found in that setting. Only 3 T-RFs were common to the supraglacial and proglacial samples. This likely reflects the fact that while supraglacially-derived waters drain through the subglacial environment, infiltrating subglacial sediments and becoming incorporated into basal ice by refreezing at the glacier bed, they are largely channelised by the time they exit the glacier and cross the glacier forefield. Thus, there are limited opportunities for them to deliver unique microorganisms to proglacial sediments. Proglacial T-RFs that were also found in the subglacial samples may have become incorporated into subglacial materials during past periods of glacier advance, or be relics of formerly more diverse subglacial assemblages most of which could not survive following glacier retreat (or be a mixture of these 2 types of organisms). Overall, Maya concluded that "*physical and chemical conditions at the bed exclude or select against certain components of the potential source communities, allow selected minor components to survive, and/or support T-RFs that cannot thrive in the surface*

environments". In short, there appeared to be a distinctively subglacial microbial community, at least at John Evans Glacier.

Table 6.1 Summary of the presence and distribution of 142 unique Terminal Restriction Fragments (T-RFs) generated by HaeIII digestion of DNA amplified for samples collected at John Evans Glacier (from Bahia *et al*., 2006).

TABLE 2. Summary of the presence and distribution of 142 unique T-RFs generated by HaeIII digestion of DNA amplified from samples collected at John Evans Glacier

Distribution of T-RFs	No. (%) of T-RFs in environment[a]:		
	Subglacial	Supraglacial	Proglacial
Total detected in each environment	104 (100)	43 (100)	50 (100)
Unique to subglacial samples	60 (58)		
Unique to supraglacial samples		12 (28)	
Unique to proglacial samples			23 (46)
Common to sub- and supraglacial samples	20 (19)	20 (47)	
Common to sub- and proglacial samples	16 (15)		16 (32)
Common to supra- and proglacial samples		3 (7)	3 (6)
Common to sub-, supra-, and proglacial samples	8 (8)	8 (18)	8 (16)

[a] Sample sites have been grouped into three broad categories to simplify comparison. "Subglacial" comprises samples from SIB, SAF, SOC waters and BT, BC and BF basal ice; "Supraglacial" comprises SS and SL stream waters; "Proglacial" includes PT and PP sediments.

After her completing her Master's degree, and following an unsuccessful move to Oxford, Maya moved to MIT/Woods Hole and completed her Ph.D. on the hydrology and organic geochemistry of part of the western margin of the Greenland Ice Sheet (more of which, later). Following a post-doctoral fellowship at the University of British Columbia, where she developed skills in genomic analysis, she returned to the University of Alberta to take up a Research Chair in 2017.

6.6 Microbiological Studies at Bench Glacier

After completing his Ph.D., Mark Skidmore held post-docs in Bristol with Martyn, and then with Brian Lanoil (now a colleague at the University of Alberta), who was then at the University of California in Riverside. I first met Brian when, as a post-doc at CalTech, he invited me to give a couple of talks about our work on glacier hydrology and biogeochemistry. He had become interested in how bacteria survived in cold environments and was starting to think about working on subglacial bacteria (and he has subsequently also worked on bacteria in sea ice, lake ice, and permafrost). His collaboration with Mark focused on new fieldwork at Bench Glacier in Alaska, where Suzanne Anderson (who I knew from my time in Seattle, when she was a Master's student there) had started a field programme investigating chemical weathering in glacial environments. In addition, with John Priscu, Slawek Tulaczyk, and Hermann Engelhardt, Mark and Brian analysed a 43 cm long sediment core from the base of

the Kamb Ice Stream in Antarctica. The latter study was probably the first direct attempt to investigate the subglacial biology of one of the world's extant continental ice sheets.

Brian, Mark and their co-workers made a direct comparison of Bench Glacier's subglacial microbial community with the community at John Evans Glacier (Skidmore *et al*., 2005). The two glaciers differed in terms of the lithologies of their underlying bedrock and the chemical composition of the waters that drained from them. The chemistry of Bench Glacier meltwaters suggested a weathering system dominated by sulphide oxidation and carbonate dissolution (similar to that of waters from Haut Glacier d'Arolla), while that of John Evans Glacier waters suggested that most of the bedrock-derived component of the solute flux was derived by dissolution of carbonates, gypsum, and anhydrite.

At Bench Glacier, they collected samples from an ice-marginal stream, from the bases of two boreholes that reached the glacier bed and intersected subglacial streams, from the basal ice layer of the glacier, and from water draining through sediments on the valley-side and valley floor. At John Evans Glacier, the samples came from basal ice exposed along the glacier margin, supraglacial and subglacial meltwaters, and subglacial and proglacial sediments. The microbial communities were characterised using clone libraries and dot-blot hybridisation of 16S rRNA genes. Despite the significant distance between the 2 sites and the differences in bedrock geology, some phylogenetic groups (including the *Betaproteobacteria*) were common to both sites, while others were unique to one or other of the sites.

Each glacier hosted a distinct population of subglacial microbes with a composition that reflected the geochemistry of the waters draining from the host glacier. Examples include sequences related to *Gallionella ferruginea* or the genus *Thiobacillus*, which were abundant in samples from Bench Glacier, but absent from samples from John Evans Glacier. These organisms are involved in the cycling of iron and/or sulphur and their presence at Bench Glacier is consistent with the inference that sulphide oxidation is a key process of weathering at that site. Equally, their absence from John Evans Glacier is consistent with the argument that sulphate in samples from that glacier is derived from dissolution of gypsum and/or anhydrite. A surprising finding, however, was that no sample from either glacier contained clones related to any known sulphur-reducing bacteria (even though such bacteria had previously been cultured from samples of basal ice and meltwater from John Evans Glacier). This may reflect the fact that clone libraries are not very effective at detecting rare organisms that may, nonetheless be a geochemically significant component of the microbial community. At both sites, the subglacial water samples contained elements that were significantly enriched relative to samples from supraglacial waters, basal ice, or subglacial sediments, all of which might be expected to contribute microorganisms to the subglacial waters. This strongly

suggested the existence of an endogenous subglacial microbial community that thrived in permanently cold, dark, and oligotrophic conditions and that could survive temperature oscillations across the freezing point, and (potentially seasonal) cycling between oxic and anoxic conditions.

6.7 The Bed of Kamb Ice Stream

Given that everyone who was looking for microbes in glaciers seemed to be finding them wherever they looked, the time was ripe to make a direct attempt to find out whether or not they were equally abundant in ice sheet settings. Brian, Mark and their collaborators made a first start at this with their study of the short sediment core from the base of the Kamb Ice Stream (Lanoil *et al*., 2009). Barclay Kamb and Hermann Engelhardt had accessed the ice stream bed by hot-water drilling and recovered the core from the base of the borehole in the 2000-2001 Antarctic field season. Previous discussion of the potential to find life at ice sheet beds had revolved largely around the suitability of subglacial lakes, such as Lake Vostok, as a potential microbial habitat. This was the first attempt to find life in a location deep in the ice sheet interior where the ice sheet was in direct contact with the underlying mineral substrate. It was thought that this substrate was likely saturated with fresh water (like a wetland) and probably overlain by a meltwater drainage system that included lakes and active drainage pathways. It was also thought that the location had been ice-covered and isolated from the atmosphere for at least 400,000 years.

Cell counts on sediment samples yielded on the order of 10^7 cells g^{-1} of sediment, which is 1-2 orders of magnitude higher than had previously been found in other subglacial settings. This might suggest some augmentation of the microbial populations by growth during storage of the core. Only a small proportion of the cells present proved to be cultivable under aerobic conditions at room temperature on R2A medium (which has a relatively low organic content). However, the culturability of organisms increased somewhat in incubations at 4 °C that were continued for more than 3 months. Incubations conducted under anaerobic conditions failed to produce growth at either temperature. It was not clear whether this indicated a lack of viable heterotrophic anaerobic organisms in the sediments or a lack of electron acceptors in the medium.

By contrast, isolates from the aerobic 4 °C plates grew well at 9 °C, and nearly half of them also did so at 25 °C. The results of microbial analyses suggested a relatively simple community containing both chemolithoautotrophs and heterotrophs, and the presence of both iron and sulphide oxidisers. It was suggested, on the basis of these findings, that the energetic basis for the community might be lithotrophic metabolism combined with autotrophic carbon fixation.

This might explain the apparently lengthy persistence of the ecosystem despite its isolation from the atmosphere. Measurement of the organic carbon content of the sediments suggested that it was sufficient (0.5-1.5 wt. %) to sustain heterotrophic microbial activity. On the basis of these results, Brian and his co-authors argued that sub-ice sheet environments in Antarctica might contain a globally significant reservoir of prokaryotic organic carbon that should be taken account of in studies of both global carbon dynamics and sub-ice sheet weathering processes. In particular, sub-ice sheet environments might support an assemblage of microbes that includes *Gallionella*- or *Thiobacillus*-like organisms that obtain energy from chemoautotrophic oxidation of sulphide minerals and/or iron. In that sense these environments seemed very similar to those already identified beneath much smaller glaciers in Arctic and Alpine settings.

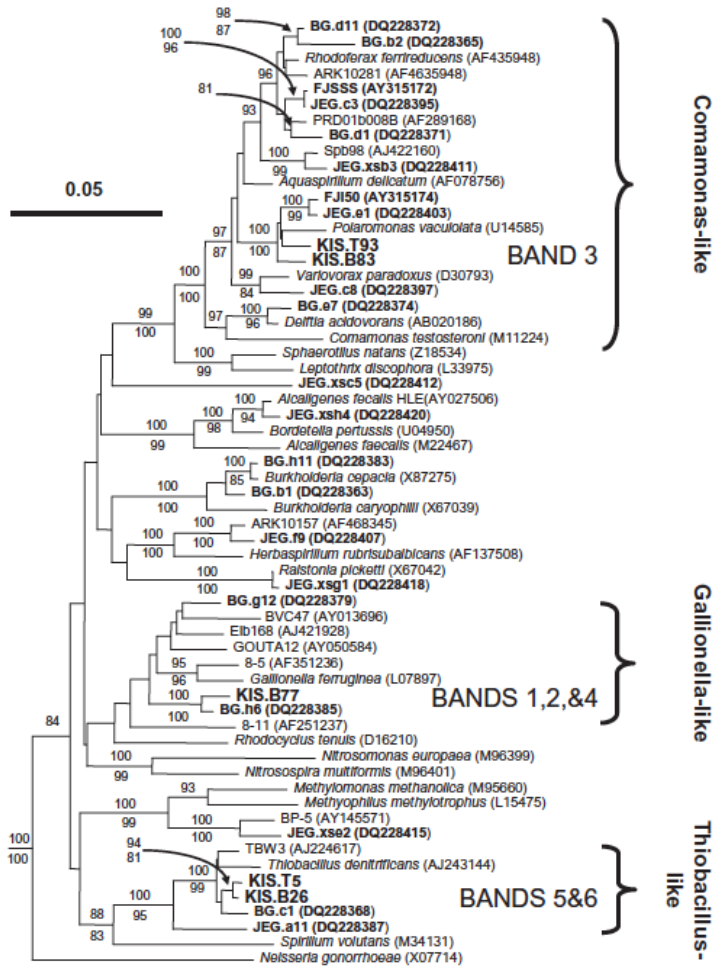

Figure 6.8 Phylogenetic tree showing the relationship between sequences obtained from sediment samples from the base of Kamb Ice Stream (bold, and labelled KIS), sequences from other subglacial systems (bold; BG = Bench Glacier; FJ = Franz Josef Glacier; JEG = John Evans Glacier) and public databases. Names of characterised isolates are italicised; uncultivated clone sequences or uncharacterised isolates are in plain text. Genbank accession

numbers are included after the names. Sequences corresponding to DGGE bands are indicated. Bootstrap values (100 replications) generated by the neighbour-joining method are shown above relevant nodes, and those generated by maximum parsimony analysis are shown below; only bootstrap values above 50 are shown. Scale bar indicates 5 conserved nucleotide changes per 100 base pairs. The tree is rooted with *Escherichia coli* (JO1695) (from Lanoil *et al*., 2009).

6.8 Microbial Export from the Greenland Ice Sheet

In a more recent study, led by Ph.D. student Ashley Dubnick, and conducted in southwest Greenland, we started to explore whether we could monitor the characteristics of microbes exported from the Greenland Ice Sheet in summer meltwater runoff as a means of characterising the seasonal evolution of the meltwater drainage system within the ice sheet (Dubnick *et al*., 2017). This was essentially an application of Maya Bhatia's finding that the microbial communities found in supraglacial, subglacial and extraglacial ice-marginal environments were distinctly different from each other. If this was also true on the Greenland Ice Sheet, then microbes might serve as natural passive tracers for runoff sources and transport pathways through the ice sheet. Studying microbial export from the ice sheet was also of interest because of its possible influence on biogeochemical processes in downstream terrestrial, fjord, and marine aquatic ecosystems.

This work was a collaboration with Brian Lanoil in Alberta and Jemma Wadham's group in Bristol. It was intended to explore (a) whether the ice sheet's meltwater drainage system evolved over time in a manner similar to the meltwater drainage systems we had studied in large valley glaciers, and (b) whether temporal changes in the balance of meltwater sources (*e.g*., supraglacial snowmelt, ice marginal snowmelt, melt of glacier ice, flushing of subglacially-stored water, and basal ice melt) and the dominant flow pathways resulted in obvious and significant changes in the composition of the microbial assemblages exported in the meltwater. The study was carried out at the glacier Kiattuut Sermiat, which was accessed by a lengthy walk every day, so the fieldwork kept Ashley lean and hungry. It built on the foundation established by our work on the seasonal evolution of englacial/subglacial drainage systems at Haut Glacier d'Arolla, Austre Broggerbreen, and John Evans Glacier, and on the pioneering work on the composition of microbial assemblages in different glacial sub-environments by Mark Skidmore, Maya Bhatia, Julia Foght, and Brian Lanoil.

The study had three main components (i) to monitor (continuously) the meltwater discharge from the glacier and its electrical conductivity (a proxy for its total solute content), (ii) to collect daily water samples from the meltwater stream exiting the glacier for chemical analyses which

we would use to characterise drainage pathways through the ice sheet and how they changed over time, and (iii) DNA sequencing and characterisation of the microbial assemblages exported from the ice sheet in runoff. These measurements were conducted from the start of May to mid-August 2015.

The primary conclusions of this work were (a) that the most important control on the make-up of the microbial assemblages exported from the glacier was whether or not the runoff had passed through the subglacial environment (as this added a unique and distinctive component to the exported assemblages), and (b) that the water source (supraglacial or extra-glacial), and the amount of time that the water spent in the subglacial environment were second order controls (implying that these environments also have some potential to influence the microbiology and biogeochemistry of environments beyond the ice sheet margin). The implication of this was that there was a close connection between the structure and functioning of the glacier drainage system, the sources of water input to that system, and the assemblage of microbes exported to downstream environments. In effect the microbes served very well as passive hydrological tracers that allowed us to build a basic model of the structure of the meltwater drainage system of the ice sheet and its structural evolution over the course of a melt season.

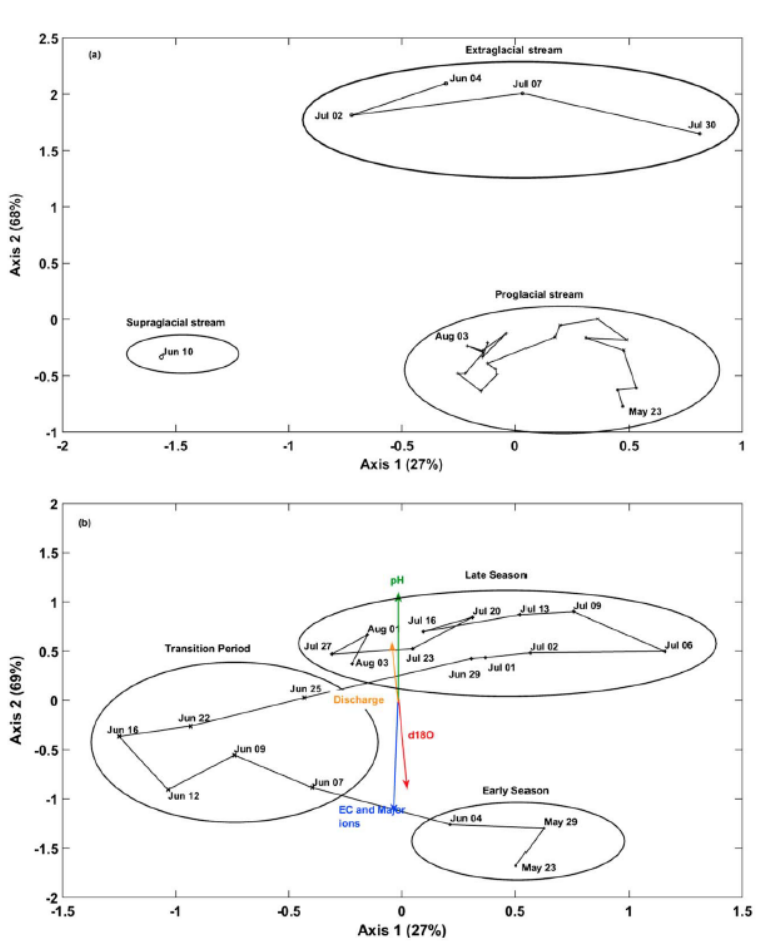

Figure 6.9 Microbial assemblage composition determined by nonmetric multidimensional scaling (NMS) ordination of Bray-Curtis distance measure using 16S rRNA gene sequencing (stress = 0.06). Values in parentheses next to axis labels indicate the percent of variance in the distance matrix explained by each axis. Multiresponse permutation procedure (MRPP) reveals significant differences between the microbial assemblages in **(a)** proglacial, supraglacial, and extraglacial meltwater streams at Kiattuut Sermiat (1000 subsamples) and **(b)** the proglacial stream in the Early Melt Season (when runoff is limited), the Transition Period (when subglacial runoff increases strongly and a diurnal runoff cycle develops), and the Late Melt Season (when subglacial runoff is consistently high with large diurnal variability) (2500 subsamples). Coloured arrows represent significant correlations with physical properties of the meltwater draining from the glacier derived using using Mantel tests ($P < 0.001$) (modified from Dubnick *et al*., 2017).

6.9 Svalbard Glacier Biogoechemistry (MT)

Austre Brøggerbreen. There were many parallels between Martin's work in the Canadian Arctic and my work on Svalbard. We kept in touch over the years and traded ideas, even though we were on different continents. Why Svalbard? We had been working on the first Arolla Project for about a year, when Mike Clark and Angela Gurnell encouraged me to start thinking about other types of glaciers. They were once again very generous and invited me to co-supervise another Ph.D. student, Andy Hodson, destined to become a Professor at the University of Sheffield and UNIS. Mike and Angela had good links with the Norsk Polarinstitut (NPI), and arranged for Andy to work on a small Svalbard glacier, Austre Brøggerbreen. Svalbard seemed like a long way away to me and the logistics seemed horrible, but we didn't know very much at all about the hydrology and hydrochemistry of the polythermal-based glaciers that were found there, and this seemed like a great thing to do. Some glaciers on Svalbard are cold-based, and so are frozen to the bed year-round, wherever the ice thickness is less than 180 or so metres. Polythermal-based glaciers have cold margins that are frozen to the bed, with a core of warm ice at the bed beneath thicker ice. Andy showed great determination (and still does) to set up and run the pioneering studies at Austre Brøggerbreen (Hodson *et al*., 2002). Mike and Angela made the good call that Andy needed to understand how discharge co-varied with meteorological forcing, since there were periodic shifts in wind fields over Svalbard and warmer, oceanic air often flowed over the archipelago from the west and south. They also felt that the suspended sediment characteristics were likely to be very different from the alpine glaciers we'd studied previously, because of the presence of permafrost in the valley sides and proglacial zone.

Andy set up continuous discharge and suspended sediment sampling of Austre Brøggerbreen runoff, and walked the glacier to determine the supraglacial hydrology that dominates small Svalbard glaciers. It is very common for the supraglacial streams to flow off the glacier and along its margins near the contact with the sidewalls, since moulins are relatively uncommon on the smaller glaciers. There was a small health and safety problem associated with working in Polar Bear country, so he learnt to carry and fire the then ancient rifles that NPI supplied. Andy showed great initiative and fortitude to come home with some great data sets. Austre Brøggerbreen is quite a small glacier, which has become even smaller recently because of climate warming. It had a polythermal basal temperature regime in the 1990s, as most of the ice around the glacier margins and in the ice tongue leading to the terminus was too thin to prevent the glacier sole from freezing to the substrate. However, the ice in the upper centre of the accumulation zone was thick enough to support a core of warm basal ice at the pressure melting point.

The first thing of note that Andy found was a moulin that appeared to be routing perhaps 0.1 m^3 s^{-1} of supraglacial melt down to the bed, just below the glacier's equilibrium line. It was thought, at the time, that water could not flow through cold basal ice that was frozen to the bed. What was happening to this water if it wasn't flowing through the cold ice? We predicted that the runoff would contain very little SO_4^{2-}, since there was only a small distributed drainage system, if we assumed that somehow the water would make it through the frozen margin. We predicted no SO_4^{2-} if the frozen basal ice was impenetrable (Tranter *et al*., 1996). The former proved to be the case, and it provoked some discussion of how the water either penetrated or flowed beneath the cold basal ice seal at the bed.

Scott Turnerbreen. Julian Dowdeswell was at Cambridge Geography, and invited me to join him on a trip to Scott Turnerbreen with his Ph.D. student, Richard Hodgkins. Julian had teased me about working on an "*insignificant cube of warm ice in the Alps*", when most of the world's ice was thicker and colder. I thought that he was definitely correct about the latter. Scott Turnerbreen is another small Svalbard glacier, but it is quite thin, so is cold-based and totally frozen to the bed. Haut Glacier d'Arolla is one end member, being entirely warm-based, and Scott Turnerbreen is the other end member, being entirely cold-based. We confidently predicted that there should be no SO_4^{2-} in the runoff. Richard collected samples from the start of the melt season through the summer to prove just this. The results were very interesting, and, of course, contrary to what we expected. There was relatively high SO_4^{2-}, and even high pCO_2 in the early season runoff, but these values gradually dropped down to low values as the melt season advanced.

It seemed unlikely that the SO_4^{2-} could come from sulphide oxidation in sediment crushed at the bed (Hodgkins *et al*., 1997, 1998). However, the terminus of the glacier contained naled ice or aufeis, solute–rich ice that forms from waters draining from the glacier terminus over winter, suggesting that water was flowing from a subglacial reservoir during the winter. The geophysics of Scott Turnerbreen suggested that the ice was below the pressure melting point throughout the glacier, and yet the water chemistry suggested that sulphides were oxidising somewhere that was wet throughout the year, since SO_4^{2-} was found in the runoff throughout the ablation season (Fig. 6.10). A distinguishing feature of Scott Turnerbreen was the wet muddy slurries that oozed over the glacier, arising from the frost shattered shale in the side walls. The pore waters in the slurry were solute-rich, and carbonation of carbonates occurred in the marginal channels on the glacier surface that carried the slurry in turbid suspension to the glacier terminus. Sulphide oxidation and carbonate dissolution also occurred, but they occurred on the side walls and within supraglacial channels that were in free contact with the atmosphere. The overall rate of chemical weathering was low (see below), but nowhere close to zero (as was formerly believed to be the case for cold-based glaciers). Richard had a great field eye, and stitched all this together himself, and with a little prod from a very helpful reviewer of the work we submitted to Hydrological Processes (Hodgkins *et al*., 1997, 1998).

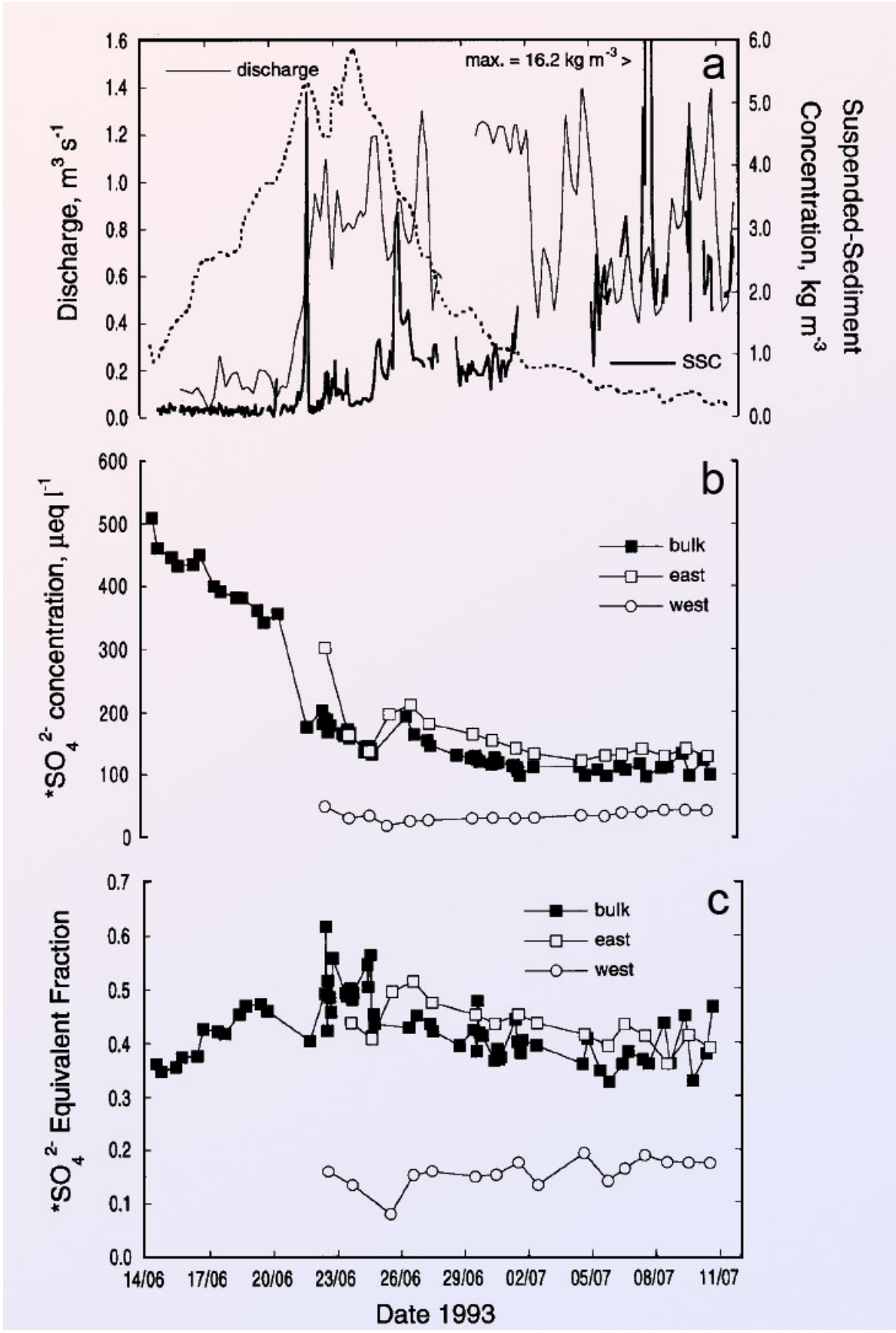
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Figure 6.10 Runoff chemistry from Scott Turnerbreen in 1993. There are significant concentrations of non-sea salt SO_4^{2-} present, and this cannot come from subglacial weathering (modified from Hodgkins, 1997, 1998).

Finsterwalderbreen. Julian's observation that more attention should be turned to larger polythermal ice masses played on my mind, and so I took the chance to turn my attention to this when Bristol gave me a Ph.D. studentship to work on Finsterwalderbreen, a larger polythermal-based glacier on Svalbard. I advertised the studentship and received a phone call from Martin, who told me that one of his undergraduate students who had done her final year dissertation on Arolla boreholes was applying. Jemma Wadham had a reputation for breaking things that couldn't be broken, but Martin said that she was very bright and driven. I confess to being very frightened when I interviewed her. My main thought was that I needed to up my game because she was much brighter and knew tons more than I did. That has remained the case over our 20 something years of collaboration. She was a natural researcher, and set about undertaking her Ph.D. with gusto. Finsterwalderbreen is a surge-type glacier, and she worked on it during the quiescent stage of the surge cycle (Raymond, 1987). Snow and ice were accumulating at the top of the glacier, forming a big bulge in the glacier profile. It was thought that evolution of the glacier drainage system held the key to when a surge started. High water pressures in an expanding distributed drainage system beneath thickening ice and snow in the accumulation zone was the recipe to start a surge. One of our missions was to look at year-on-year variations in both the hydrology and the hydrochemistry, searching for a proportionally bigger and bigger component of flow that arose from the distributed drainage system.

Jemma has a knack of being in the right place at the right time with the right people. She found big differences in the hydrology and hydrochemistry between the two field seasons (Wadham *et al*., 2001). The first, warmer, field season in 1994 was eventful in that there seemed to be an "outburst" from the glacier - a sudden large increase in discharge without any obvious meteorological forcing (Fig. 6.11). Remarkably, solute concentrations in the runoff did not decrease by too much during the outburst, unlike at HGA, where increases in discharge were associated with significantly more dilute runoff. There was no outburst during the second, colder summer season in 1995, but there was evidence of pressurised water upwelling from the proglacial sediment. The pressurised water had the sea salt signature of the snowpack, and the chemical weathering signature of weathering in a distributed drainage system. This was evidence that pressurised waters at the bed of the glacier were able to flow through the subglacial debris, and beneath the permafrost that otherwise froze the margins of the glacier

to the bed (Wadham *et al.*, 1998). Relatively warm years produced copious melt that was able to hydro-fracture the frozen seal and produce outbursts, while colder years could initially produce only sub-permafrost flow. The outburst in the cold season occurred at the end of summer, presumably when subglacial water pressures were sufficient to hydro-fracture the marginal frozen ice seal.

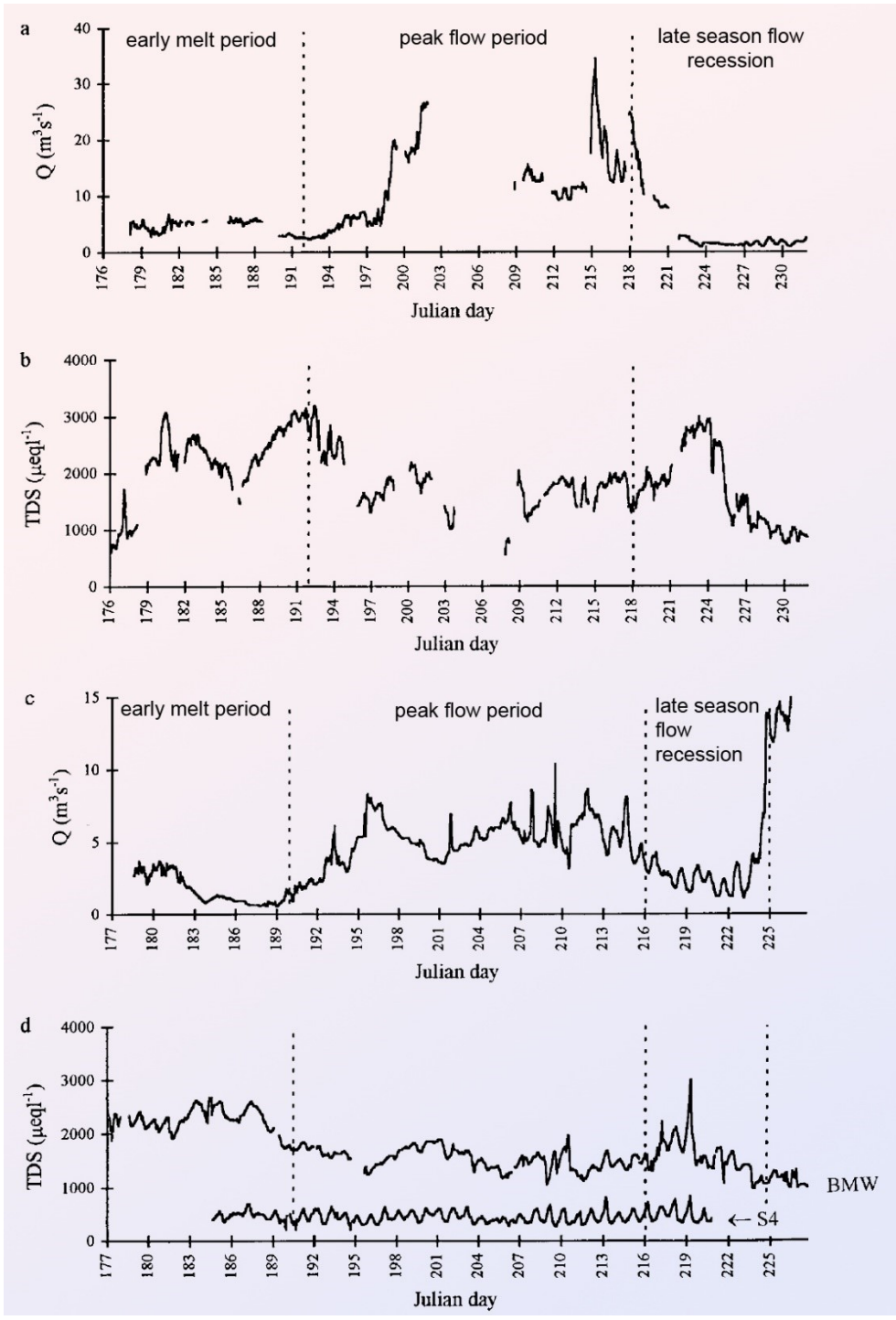

Figure 6.11 Contrasting hydrographs for two melt seasons at Finsterwalderbreen (modified from Wadham *et al.*, 2001). The first hydrograph shows a summer outburst in a warmer melt

year, when discharges was relatively high, whereas the second hydrograph shows a late melt season outburst in a colder melt year, when discharges were relatively low.

An interesting geochemical observation was that, once again, sulphide oxidation and carbonate dissolution were the principal biogeochemical weathering reactions in the subglacial environment (Wadham *et al*., 1998). This made sense, in that the fundamentals of glacial erosion are the same beneath glaciers worldwide, carbonates and sulphides are trace minerals in many silicate rocks, and glacial comminution releases these minerals from their silicate mineral matrix. We started to wonder whether the geochemical processes at the bed of our little warm ice cube in the Alps could be extrapolated to bigger glaciers worldwide. Larger glaciers have longer subglacial flow paths, and there is more likelihood that anoxia will occur along them if sulphide oxidation and microbial respiration are occurring. Jemma and I noticed that there appeared to be excess CO_2 in some of the concentrated upwelling waters (Wadham *et al*., 2000), and I received funding to employ her as a post-doc to undertake stable C and S isotope studies of these waters, along with Simon Bottrell at Leeds.

Finsterwalderbreen has an anoxic bed. Simon is a great isotope geochemist, and nothing was a problem for him. We devised a scheme to sample the ice marginal stream and the subglacial upwelling in the summer of 1997, and the subglacial upwelling again in the late winter of 1999, obtaining samples for $\delta^{13}C\text{-}HCO_3^-$, $\delta^{18}O\text{-}H_2O$, $\delta^{18}O\text{-}SO_4^{2-}$ and $\delta^{34}S\text{-}SO_4^{2-}$. The results were rather startling (Wadham *et al*., 2004). The sulphate mass fraction, (SMF: $SO_4^{2-}/(SO_4^{2-} + HCO_3^-)$ is 0.5 (using units of equivalents, rather than moles) when sulphide oxidation coupled to carbonate dissolution is the dominant biogeochemical weathering reaction giving rise to the HCO_3^- and SO_4^{2-} in solution (equations 2.4 and 3.5). The winter upwelling water (Wadham *et al*., 2000) are rich in Cl^-, and have SMFs around 0.5 (Fig. 6.12a), testimony to snowmelt draining through a distributed drainage system. However, the $\delta^{34}S\text{-}SO_4^{2-}$ was enriched in ^{34}S (Fig. 6.12b), and the $\delta^{18}O\text{-}SO_4^{2-}$ showed evidence of sulphate reduction (Fig. 6.12c). Finally, all the $\delta^{13}C\text{-}HCO_3^-$ values were depleted in ^{13}C. This suite of characteristics is diagnostic of a subglacial drainage system that is driven anoxic by oxidation of organic matter, which gives rise to depleted $\delta^{13}C\text{-}HCO_3^-$ (Fig. 6.12d).

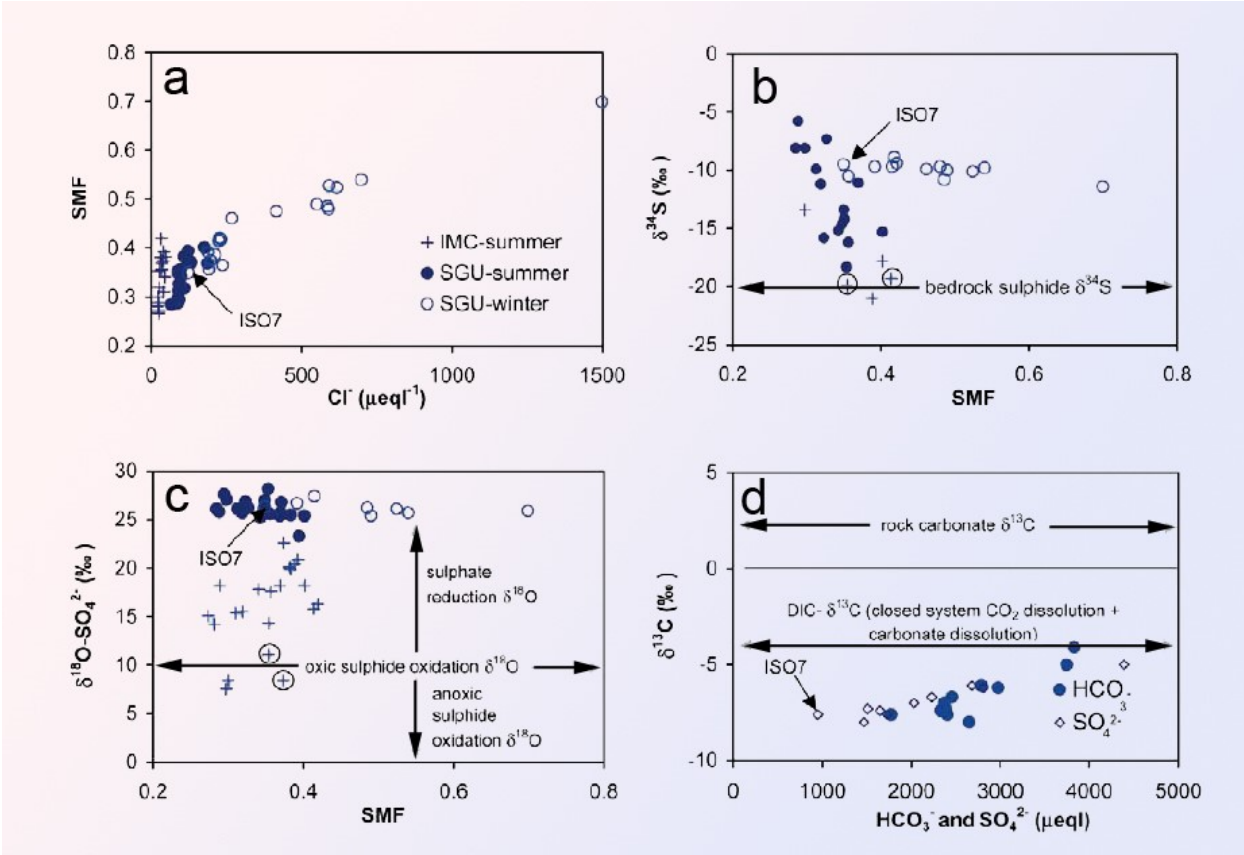

Figure 6.12 Chemical and isotope characteristics of subglacial meltwaters upwelling in the fore field of Finsterwalderbreen (modified from Wadham *et al*., 2004). The isotope variations all point to the SO_4^{2-}, produced by oxidation of sulphides, being reduced back to sulphide further along anoxic water flow paths beneath the glacier.

We speculated on the possible sources of the organic matter, which were likely to be either necromass (dead microbes washed downstream by water flow), or organic matter in the shale. My hunch has always been that it is the latter, but we could not distinguish between the two with the tools and samples available to us at the time. However, we showed that waters passing through longer drainage pathways became increasingly anoxic (Fig. 6.13), and this shaped our thinking for much of the work we undertook on ice sheets.

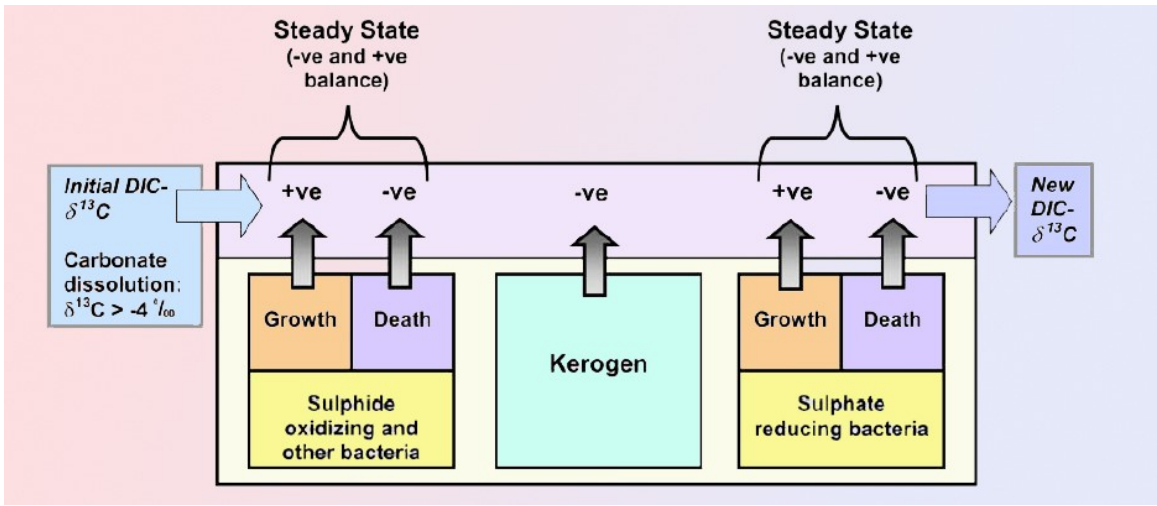

Figure 6.13 The impact of microbial processes on the isotopic composition of dissolved inorganic carbon beneath Finsterwalderbreen.

Jemma applied for, and was shocked (Martin and I weren't….) to get a lectureship in Bristol Geography, and she has had the misfortune to be in the same School as her ex-Ph.D. advisor ever since. It was great for me, because we had overlapping interests, but very different takes on how to achieve research goals. Richard Hodgkins applied for a Lectureship in Royal Holloway, and got it, and Andy Hodson did the same at Sheffield, after a year of working as a tutor at Oxford Geography. Our first combined joint grant application was to return to Finsterwalderbreen and examine chemical weathering in greater detail, looking for evidence of CO_2 draw-down or release (see below). Jemma and I were awarded a studentship by Bristol Geography, and we appointed Richard Cooper, an undergraduate from Royal Holloway who Richard H. had nicknamed "Two Brains". We snapped him up. He too had drive, insight and imagination.

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Text Box 6.1 – Slettebu and the deer which came to visit

NPI had established a hut, called Slettebu, on the fjord coastline in front of Finsterwalderbreen, and this was occasionally visited by polar bears. We had several visits from them over the years. One of the more famous ones involved Richard C. assuming that there was a reindeer watching him record discharge from the other side of the main channel draining Finsterwalderbreen. He was stone cold sober. He is quite short-sighted, and without glasses, he can just about tell the difference between a mountain and a river. He had taken off his glasses to download a data logger, and he was a little shaken to see that the reindeer trying to cross the stream was a fully grown polar bear. He fired a rifle shot over its head to

persuade it to turn around, and then ran back to Slettebu to raise the alarm. We were well prepared early the following morning when it came looking for breakfast, which was us. We were able to ward it off using a combination of trip wire flares and frying pans making a din on the wooden walls of the hut – polar bears hate loud noise - and send it down the fjord to look for food, that wasn't us.

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Groundwaters in the proglacial plain of Finsterwalderbreen. The walk to the terminus of Finsterwalderbreen was through a haphazard mixture of bumps and depressions in the moraine field left by previous glacier surges. Richard C. and Jemma noticed that there were very different conductivities in the small streams draining from the different small depressions in the moraine field, and I noticed that some of the dark dry shale fragments on the surface of the moraine that had dried in the sun were covered with a white mineral dusting. We brought some of this white powder back to Bristol, grateful that customs did not apprehend the transit of this strange substance, dissolved it in water and found that it was largely gypsum ($CaSO_4$) (Cooper *et al*., 2002). Richard H. had been carefully constructing water budgets for the proglacial zone, and noted that water seemed to be flooding into the plain during rising discharge, and draining from it during falling discharge, rather like the channel marginal zone under HGA and the hyporheic zone of temperate stream channels (Hodgkins *et al*., 2009). We put these two observations together and figured that sulphide oxidation and carbonate dissolution must be happening in the proglacial zone, just like it did in subglacial sediments, and that evaporation was drawing up and concentrating the groundwater in some surface environments, eventually leading to the precipitation of gypsum. We had developed the hypothesis, and sent Richard C. back to the field to test it by sinking a number of groundwater wells in the proglacial plain. Jake Peters, based at the USGS in Atlanta, Georgia, was very helpful to us, giving advice on how to design, drill and establish the wells in till.

Richard C. did a great job with his wells, showing that the ground waters in the proglacial plain were much more concentrated in solute than the contemporaneous glacial runoff (Fig. 6.14), and that evapo-concentration was occurring. A nice feature of his data set was that as the waters became more concentrated, the HCO_3^- concentration decreased as a consequence of carbonate precipitation (Fig. 6.14). The same thing happens when sea water is evaporated. Suzanne Anderson had also found that sulphide oxidation dissolves carbonates in relatively young, recently exposed moraine, and that as these minerals become exhausted in older moraine, silicate dissolution driven by carbonation takes over (Anderson *et al*., 2000), and it was gratifying that our work fitted so well into that narrative.

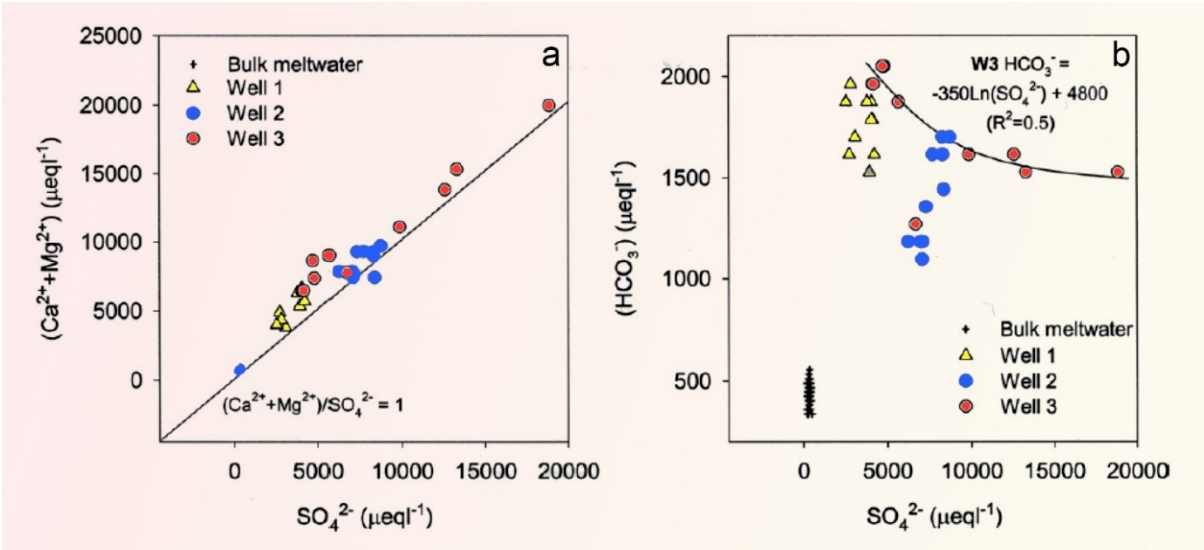

Figure 6.14 Groundwater chemistry in the proglacial sediments of Finsterwalderbreen (modified from Cooper *et al*., 2002). The waters are evapo-concentrated and precipitate $CaCO_3$, which drives them relatively rich in SO_4^{2-}.

Glaciers chemically weather bedrock everywhere. We had shown that chemical weathering was happening in cold-based and polythermal-based glaciers, which was something of a surprise to the Earth Science community, and Martin and I were very keen to place our work into the grand scheme of Earth System Science. We felt we needed to do this before anyone would fund us to work on ice sheets. We set our minds on how best to achieve this, and started to calculate chemical weathering rates for different types of glaciers. We also felt that there must be a global geochemical weathering story to tell, as water fluxes from glaciers and ice sheets change so much during glacial cycles (Sharp *et al*., 1995b). I decided to blunder into the murky world of CO_2 draw down and changing atmospheric CO_2 concentrations over glacial-inter-glacial timescales, and upset quite a few reviewers in so doing.

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7. RATES OF CHEMICAL WEATHERING IN GLACIATED TERRAIN (MT)

I love the work of Heinrich Holland (Holland, 1984), and the Chemistry of Atmospheres and Oceans (Holland, 1978) remains one of my favourite books. I am also a fan of Bob Garrels, Fred Mackenzie (Garrels and Mackenzie, 1971) and Bob Berner (Berner and Berner, 1996), but, collectively, their work contains relatively little about the potential impact of ice-related processes on global biogeochemical cycles. The Earth Science community felt that the effects were probably limited, because larger ice masses were thought to be largely frozen to the bed, and so that there could not be much water in contact with crushed minerals. If temperatures were low year round, rates of chemical weathering were also thought to be slow. Additionally, there was no soil (Gibbs and Kump, 1994). Most chemical weathering in temperate and tropical locales occurs in soil (Drever, 1997), so glaciers did not seem to have much going for them as potential agents of chemical weathering. The only positive factor seemed to be that glaciers crushed bedrock into fine silt- and clay-sized flour, which maximises the chance for it to interact with water, all other things being equal, so Martin and I set out to explore whether this gave glaciers a role in global geochemical cycles. Mark Skidmore was Martin's Ph.D. student in 1994, and he provided the spark to get us moving. Mark's initial plan was to get a quantitative understanding of which minerals provided the solute in runoff from Haut Glacier d'Arolla, and to determine how much chemical weathering the warm ice cube in the Alps was undertaking.

7.1 A First Chemical Weathering Model for Haut Glacier d'Arolla

We put our heads together on a trip I made to Edmonton early in 1995. Holland was great at breaking down what one might otherwise think of as complicated calculations into simple steps, and we applied his logical way of dissecting chemical weathering equations into rock- and atmosphere- derived solute to our first Arolla chemical weathering model (Tranter *et al.*, 1993), splitting up the amount of HCO_3^- in the meltwaters into components that arose from carbonate dissolution and from atmospheric carbon dioxide. Briefly, we assumed that the bulk of the SO_4^{2-} in meltwaters that came from sulphide oxidation and that the resulting sulphuric acid in the meltwaters would dissolve carbonates first. These processes would then account for all of the SO_4^{2-} and a large fraction of the Ca^{2+} and Mg^{2+} in solution. We assumed that the residual HCO_3^- came from carbonation of carbonates, using carbonic acid derived from dissolution of atmospheric CO_2 in the meltwaters, and that this also accounted for the rest of the Ca^{2+} and Mg^{2+}. The remaining HCO_3^-, which balanced the Na^+ and K^+, came from

carbonation of silicates using atmospheric CO_2. We summed up daily solute fluxes from the glacier into annual fluxes, and derived two values. The first was the sum of base cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}), and the second was the amount of HCO_3^{-} that was derived from the atmosphere, otherwise known as the CO_2 draw down. We normalised these values to the area of the glacier, allowing us to make comparisons with other terrestrial environments. The first thing of note was that the chemical weathering rate was 640-685 meq m^{-2} yr^{-1}, well above the continental average of 390 meq m^{-2} yr^{-1} (Livingstone, 1963). We checked out chemical weathering rates of other glacier systems that had been estimated to date, and these were 450-1000 meq m^{-2} yr^{-1}, albeit based on much less data than we used for our calculations (Sharp *et al*., 1995b). These data convinced us that it should be difficult to believe that glaciers did not chemically weather comminuted bedrock at an appreciable rate.

7.2 Rates of Chemical Weathering in Other Glacial Systems

Andy Hodson did a great job of bringing together all the work on chemical denudation in glacierised basins to date, with an emphasis on Arctic glaciers, using his own and Geir Vatne's unpublished data (Hodson *et al*., 2000). Svalbard glaciers have cationic denudation rates of 160-560 meq m^{-2} yr^{-1}. Cold-based Scott Turnerbreen came bottom of the list with 160 meq m^{-2} yr^{-1} (Hodgkins *et al*., 1997), Austre Brøggerbreen, with only a small distributed drainage system, was a little higher, at 240-270 meq m^{-2} yr^{-1} [10], while truly polythermal Finsterwalderbreen fluctuated, depending on whether or not it was a high runoff year, from 210-440 meq m^{-2} yr^{-1} (Wadham *et al*., 1997). Andy showed that high chemical denudation rates, as well as high CO_2 drawdown rates (see below), are associated with specific bedrock lithologies, with high rates being associated with basalt and carbonate bedrocks (Hodson *et al*., 2000). The continental average value of 390 meq m^{-2} yr^{-1} (Livingstone, 1963) was spanned by the rates calculated for the glaciers examined, so it was still hard to argue that glaciers were not banging their buck as chemical weathering agents. This point of view did not sit well with everyone, since where the solute comes from is a big determinant of the impact of chemical weathering on atmospheric CO_2 draw down (see below). Suzanne Anderson and Tim Drever made the point that glaciers are not good at dissolving silicate bedrock (Anderson *et al*., 1997), and it is hard to disagree with that. However, glaciers are good at dissolving carbonates (Hodson *et al*., 2000; Tranter *et al*., 2002), and that keeps the cationic denudation rate high.

7.3 Broader Implications?

It is well known that floods in large rivers carry the most sediment on a range of timescales (Karimaee Tabarestani and Zarrati, 2015), but it is less well known that the dilute waters that characterise rivers and glacial runoff at high discharge carry the highest solute fluxes. This is because the proportional increase in discharge is always greater than the proportional decrease in total solute concentration, so that the solute flux (the product of discharge and total solute concentration) increases as discharge increases. Martin made the slightly provocative comment in our 1995 *Geology* paper that meltwater discharge pulses during deglaciation might result in atmospheric CO_2 depression (Sharp *et al*., 1995b), which started us thinking about whether glacial chemical weathering could be a player amongst the other drivers of atmospheric CO_2 change, albeit on longer timescales.

7.4 A Second Model of Glacial Chemical Weathering

Our first model of chemical weathering beneath glaciers suggested that atmospheric O_2 was the limiting factor on how much sulphide oxidation could occur (Tranter *et al*., 1993), while the second model suggested that other oxidising agents, such as Fe(III), NO_3^- and Mn(IV), could also be controls, since microbes catalyse these reactions (Tranter *et al*., 2002). The first model suggested that dissolved CO_2 species were primarily derived from carbonate minerals and the atmosphere, while the second model suggested that dissolved CO_2 species could also be derived from oxidation of organic matter, and that there might be little need for atmospheric CO_2 to drive subglacial chemical weathering. This is particularly helpful since subglacial channels are often water-filled, so there is no obvious gas phase source of CO_2. These may seem esoteric distinctions, but they impact both the amount of chemical weathering that can occur and the longer-term impact of glacial runoff on atmospheric CO_2 concentrations.

Silicate and carbonate weathering draw down CO_2 from the atmosphere: Text Box 7.1 (equations 7.3 and 7.4 below) shows that CO_2 is consumed during chemical weathering, and converted to HCO_3^-. The CO_2 is not usually taken directly out of the atmosphere in many temperate and tropical weathering environments. Much of the chemical weathering happens in soils, where the CO_2 comes from root respiration or oxidation of soil organic matter. This means that most of the CO_2 is originally taken up by plants and autotrophic microorganisms during photosynthesis, and that some of the organic matter that is formed is transferred into the solution by respiration, rather being returned to the atmosphere. A large proportion of the CO_2 in deeper soil layers is used to chemically weather rocks (Text Box 7.1, equations 7.3 and 7.4).

Soil waters normally have high pCO_2, being over-pressured with CO_2 relative to the atmosphere by one or two orders of magnitude. So, when these waters re-emerge to drain

into rivers, *en route* to the ocean, a little of the CO_2 degasses (Holland, 1978) and drives up the river water pH until it roughly equilibrates with the atmosphere. Most river waters eventually discharge into the oceans, and the dissolved CO_2 species are ultimately removed by marine carbonate precipitation, which returns one mole of CO_2 back to the atmosphere for every one mole of carbonate that is precipitated (see Text Box 7.1). Thus, there is no net change in atmospheric CO_2 concentrations as a result of terrestrial carbonate weathering, although there may be lags in the balancing of this cycle.

Terrestrial silicate weathering, by contrast, draws down atmospheric CO_2 (Text Box 7.1). The residence time of Na^+ and K^+ in the oceans is long, so the carbonation that produces these species is a long-term sink for atmospheric CO_2. The carbonation of Ca^{2+}- silicates is also a sink for atmospheric CO_2, despite half the HCO_3^- being returned to the atmosphere as CO_2 during marine carbonate precipitation (Text Box 7.1).

Subglacial sulphide weathering potentially has an impact on atmospheric CO_2 concentrations, returning oceanic dissolved CO_2 species back into the atmosphere (Text Box 7.1). Sulphide oxidation, whether it results in dissolution of carbonates or Ca-silicates, leads to an increase in atmospheric CO_2 concentrations when the Ca^{2+} released from the rock minerals is precipitated as carbonate minerals in the oceans (Text Box 7.1).

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Text Box 7.1

(Equation 7.1) Terrestrial carbonate weathering and marine carbonate precipitation do not change atmospheric CO_2 concentrations.

Carbonate weathering on land Carbonate precipitation in the oceans

$CaCO_3$ (s) + CO_2 (g) + H_2O (l) → Ca^{2+} (aq) + $2HCO_3^-$ (aq) → $CaCO_3$ (s) + CO_2 (g) + H_2O (l)

1 mole of atmospheric CO_2 consumed 1 mole of CO_2 released to the atmosphere

(Equation 7.2) Terrestrial silicate weathering and marine carbonate precipitation draw down atmospheric CO_2 concentrations.

Silicate weathering on land Carbonate precipitation in the oceans

Ca-silicate + $2CO_2$ + H_2O (l) → Ca^{2+} (aq) + $2HCO_3^-$ (aq) + H_2-silicate → $CaCO_3$ (s) + CO_2 (g) + H_2O (l)

2 moles of atmospheric CO_2 consumed 1 mole of CO_2 released to the atmosphere

(Equation 7.3) Terrestrial sulphide oxidation linked to carbonate dissolution and marine carbonate precipitation increases atmospheric CO_2

Carbonate weathering on land Carbonate precipitation in the oceans

$2CaCO_3$ (s) + H_2SO_4 (aq) → $2Ca^{2+}$ (aq) + $2HCO_3^-$ (aq) + SO_4^{2-} (aq) → $CaCO_3$ (s) + CO_2 (g) + Ca^{2+} (aq) + SO_4^{2-} (aq)

Ca^{2+} (aq) + $2HCO_3^-$ (aq) → $CaCO_3$ (s) + CO_2 (g) + H_2O (l)

no atmospheric CO_2 consumed 2 moles of CO_2 released to the atmosphere

(Equation 7.4) Terrestrial sulphide oxidation linked to silicate dissolution and marine carbonate deposition increases atmospheric CO_2

Silicate weathering on land

Ca-silicate + H_2SO_4 (aq) → Ca^{2+} (aq) + SO_4^{2-} (aq) + H_2-silicate

no atmospheric CO_2 consumed

Carbonate precipitation in the oceans

Ca^{2+} (aq) + $2HCO_3^-$ (aq) → $CaCO_3$ (s) + CO_2 (g) + H_2O (l)

1 mole of CO_2 released to the atmosphere

==========

We started to think about how these combinations of equations might lead to subglacial chemical weathering perturbing atmospheric CO_2 concentrations. I became convinced, but unfortunately incorrectly, that glacier chemical weathering could have a direct effect on atmospheric CO_2 concentrations. I misunderstood a passage in another of my favourite books, Wally Broecker's *Tracers in the Oceans* (Broecker and Peng, 1982), which says that the carbonate cycle was balanced on the timescale of several thousand years. Phillipe Huybrechts, at Liege, kindly gave me access to his calculations of iceberg and melt runoff from Antarctica during the last glacial cycle, and Martin obtained similar data from Johannes Oerlemans at Utrecht. Glaciers are great at dissolving carbonate. On the assumption that the

carbonate was dissolved by atmospheric CO_2 and that other terrestrial weathering rates of carbonates and silicates remained constant, I simply lagged the drawdown of CO_2 from the atmosphere with its return to the atmosphere from the oceans by a few thousand years. Hey presto, CO_2 concentrations declined in the atmosphere as the Greenland and Antarctic ice sheets grew, and strangely, the changes in atmospheric CO_2 concentrations were quite similar to those recorded in ice cores.

I should have learned my lesson from the 2CCMM. You can't solve a complex problem with a very simple solution, particularly if the simple solution is fundamentally incorrect. I gave a few talks on this work in the UK, and we glaciologists loved it, but the earth and marine sciences communities were aghast. Thank goodness I talked to polite audiences in the UK, who were none-the-less robust in their disbelieving. I can imagine a few places abroad where I would have been burnt at the stake. We tried to publish the material in leading journals, and, thankfully, it was roundly rejected. I would have hated to be remembered as the joker who botched up glaciers and global geochemical cycles. It was a frustrating period to have lived through – you think that you have a scientific Holy Grail in your grasp, but then the pot of gold, to mix a metaphor, disappears with the rainbow. I learnt a lot about listening to well-meant criticism and acting positively on it.

I was very fortunate to have a shot of good luck. Every dark cloud has a silver lining, and the idea that we needed to know more about chemical weathering beneath ice masses had a resonance in our peer group. Martin was instrumental in grounding my flights of imagination and helped rebrand a NERC grant application to work in Greenland for three years. Mark Skidmore came to work with me as a post-doc on the field and lab side, and Guy Munhoven received an EU Fellowship to come and work with us on the impact of glacial weathering on the marine carbon cycle. This set in motion my move away from working on small warming ice cubes in the Alps, and even the larger colder ones on Svalbard, to the might of the Antarctic and Greenland Ice Sheets.

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8. MOVING TO THE GREENLAND AND ANTARCTIC ICE SHEETS (MT)

8.1 Bristol Glacier, SW Greenland

The Greenland Ice Sheet is a big place, and having funding to work at just one site required some skill in finding just the right site to study. Mark Skidmore had been through this exercise working on Ellesmere Island, and he was appointed as the post-doc on the project. Logistics and cost are key to where you first start working in a remote place, and we had two other criteria to match. We wanted to work on the most unreactive bedrock we could find, ancient crystalline continental shield, and at a site with as few small valley glacier characteristics that we could find. We had to work on land terminating ice, because of sampling, living, and cost considerations. Mark chose a site on the SW margin of the Ice Sheet (Fig. 8.1), about 70 km to the north of Kangerlussuaq (Statham *et al.*, 2008). The site was absolutely fantastic, the glacier terminus being only a kilometre or so down a small valley from the main body of the ice sheet. However, a significant difficulty for us was the size of our budget and the cost of helicopter for personnel changes and re-supply. We were to be in the field for ten weeks in the summer of 1999 with only a put in, a pull out and two mid-season re-supplies. I could write a novel about the incidents that occurred during that field season, but here are the highlights, before I continue with the science.

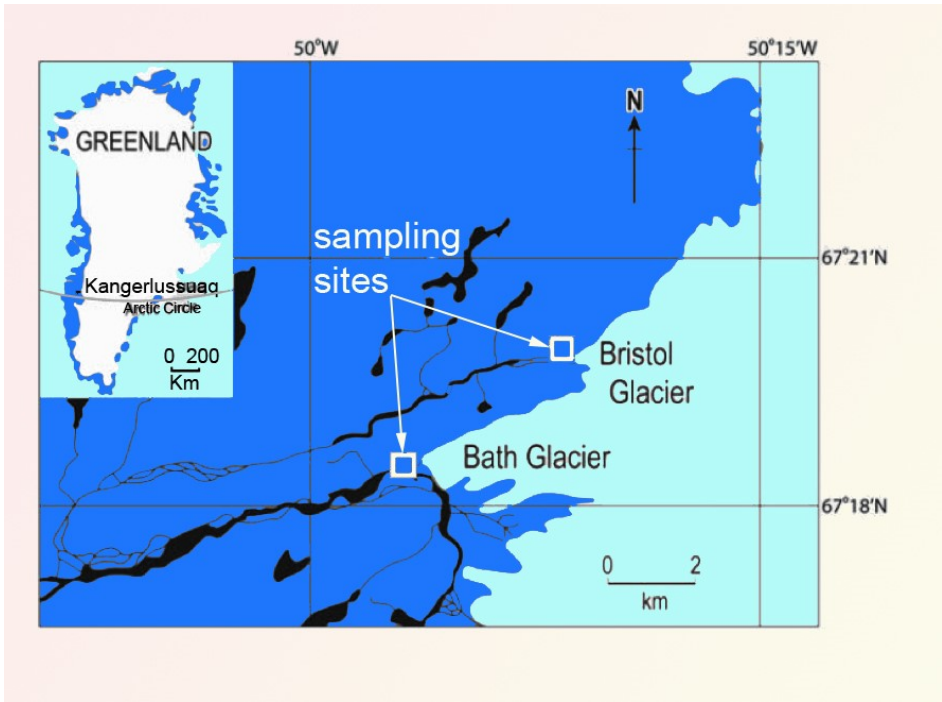

Figure 8.1 The location of Bristol Glacier, SW Greenland (modified from Staham *et al.*, 2008).

Our team was Mark Skidmore (Skids), new Ph.D. students Allan Wynn Jones and Amy Jackson, and a Ph.D. student of Pete Nienow's, Karen Grust. Skids was our ultra-anal Fe man. The proglacial environment was very windy and dusty, and the potential for Fe contamination was everywhere – in the air, dust in your hair and clothes, to name but three. Mark banned us from his analytical tent. He largely shed his outdoor clothes and boots in the entrance to the inner tent, and took on the attributes of a naked mole rat (there is such an animal…) to get his analysis done. He put together a great data set, and hats off to him. Alan Wynn was our Ge/Si person. He hadn't really been in the field before, but had done a lot of walking in the North Wales hills near to where he was born and grew up. Amy Jackson looked after solutes and suspended sediment, and Karen was the person with the huge task of measuring discharge.

8.2 The Helicopter Ride to Oblivion

The helicopter ride to the site, some 70 km north of Kangerlussuaq, was incredible, and one I have never forgotten. Mark was in the front with the pilot guiding him to our site. The site had no name, so we eventually called it Bristol Glacier. I was knocked out by the scale of the ice sheet – the little warm ice cube in the Alps was just that, compared with the sea of fractured ice margin we flew over. Our Swedish pilot was looking forward to flying low over the ice, and had promised us some great views. We flew over the bowl of a huge supraglacial lake that had drained recently, and the pilot became excited. There was a huge moulin at its base, and at least two ice pillars rising from the base to just below the ice surface. I estimate that they were 20 m plus in height. I knew that the drained lake bowl was large, but I still remember the sinking feeling in my stomach when the helicopter descended to take a closer look inside it. The two air hostesses didn't look so happy either, and strapped themselves in. Next, we were below the surface of the ice sheet stunting in a big helicopter around the ice columns. I remember thinking that we were dead if we hit anything, because the moulin was so large that the helicopter wouldn't have touched the sides of it when it crashed and skidded down to the lowest part of the lake. I thought that Skids had set this up with the pilot to frighten me - it had. We flew out in one piece thank goodness, and landed eventually at Bristol Glacier. I would quite happily have killed Skids and the pilot, but we needed the pilot to come back to get us, so I mentally settled on killing Skids. My memory of Skids walking out of the cockpit is one for my death bed – he looked grey with fright, and could only mutter "*the guy's a nutter….*". The stage was set for an eventful summer.

The field season was the toughest I have ever undertaken. The environment seemed to be hell bent on driving you away so that it could retain its secrets. The katabatic winds blew from the ice sheet a lot of the time, and the wind was enough to chill you to the bone. I seldom felt warm, except when sheltering behind boulders at lunchtime in the sun, and after about 15 minutes in my sleeping bag at night. There were moments that could last as long as 45 seconds when the katabatic winds stopped, and the place was warm and just beautiful, but then dark clouds of mosquitos would rise from the grasslands surrounding the proglacial plain, and you knew you were on their menu. I didn't quite crack from the environmental pressure, but I can easily understand how wind and biting insects can unhinge you. Several evenings in my tent, pitched by the melt stream in front of the glacier, left me swearing at breakfast the following morning that I had heard the best rock music imaginable coming from the water.

8.3 Ice Sheet Outburst

The small stubby glacier that Skids had chosen had a steep slope down to a cliff-like terminus, and the terminus had a huge portal in it that had mostly frozen up. There was just a little water flowing from it when we arrived. What struck us was the size of the rounded boulders in the stream bed. The rock marbles ranged from 1-3 m in diameter, and all Skids and I could think about was how much water would be required to move and round the large marbles (Figs. 8.2 and 8.3). We also thought about the outbursts from John Evans Glacier (Skidmore and Sharp, 1999) and Finsterwalderbreen (Wadham *et al*., 2001). We knew that there must also be outbursts from the ice sheet to produce these large, rounded boulders, and that we did not want to be anywhere in the vicinity of the stream bed when this happened.

The first couple of weeks of the field season were odd. The weather started to warm and we could see the streams on the glacier surface starting to flow. We observed crevasses either full or filling with water when Karen led us onto the glacier for recces. However, there was relatively little discharge from base of the huge frozen portal. Karen undertook some dye tracing experiments and showed that the discharge was being fed mostly by water produced by melting near to the terminus. We had little to do other than to wait and observe what happened next, but we knew an outburst was coming. The conductivity of the runoff was not what I had anticipated – it was dilute, with initial conductivities of 40 μS cm^{-1}, largely coming from permafrost melt from organic-rich soils on the surrounding valley sides, falling to 20 μS cm^{-1} in no time at all as melting occurred near the terminus. I had anticipated that we should be getting concentrated subglacial discharge, with values over 100 μS cm^{-1} as at the bed of Haut Glacier d'Arolla, and I admit to being very disappointed. I could not see how dilute glacial runoff would have any influence on atmospheric CO_2 concentrations. Water chemists like

water with lots of solute in it to allow the measurement of all sorts of compounds, and instead, we had this rather dilute stuff to play with. I felt deflated.

Things changed after a couple of hot days (Fig. 8.4), during which Skids and I were becoming increasingly agitated about the lack of discharge, despite the large amount of melting we could see on the ice sheet surface. Ian was a regular early riser and lover of porridge. He always had a cheery disposition, and always got up first to make the breakfast. He'd set us up for another day of sampling, when Skids noticed two cracks in the front of the glacier terminus that were spouting water. They weren't quite John Evans fountains (Skidmore and Sharp, 1999), but there was certainly water flowing from hydro-fractured ice. We were all excited. The discharge was going to rise. Skids and I ran to the glacier with our sampling kit, but then saw the marbles. We had the mother of all stage fright, well death fright to be honest. What would happen if the ice plug in the portal broke and the outburst either took us or cut us off from the camp side of the valley? Karen, characteristically, told us to man up. She would come and get us from the far side of the stream by traversing the front of the glacier with kit if needs be. We just about convinced ourselves that the outburst would start slowly and get progressively bigger over time, just as when the Gornersee drains catastrophically at the Gornergletscher. We traversed the melt stream very nervously in front of the portal, donned our hard hats, and sampled the waters pouring out of the hydro-fractures. We were so nervous, and yet so hugely excited, it wasn't true. The EC of the meltstream was <20 μS cm^{-1}, and the hydro-fracture water had conductivities of 38 μS cm^{-1}. We had just sampled what we believed to be concentrated overwinter stored water. We didn't want to stay very long in what we felt was a very dangerous place, so we collected about 10 litres of water and more or less ran back through the melt stream like two schoolboys who had just robbed a sweet shop.

Figure 8.2 Mark Skidmore sampling early season runoff in front of Bristol Glacier, Greenland, June 1999.

Figure 8.3 Mark Skidmore sampling runoff, some distance from the front of Bristol Glacier, Greenland, July 1999.

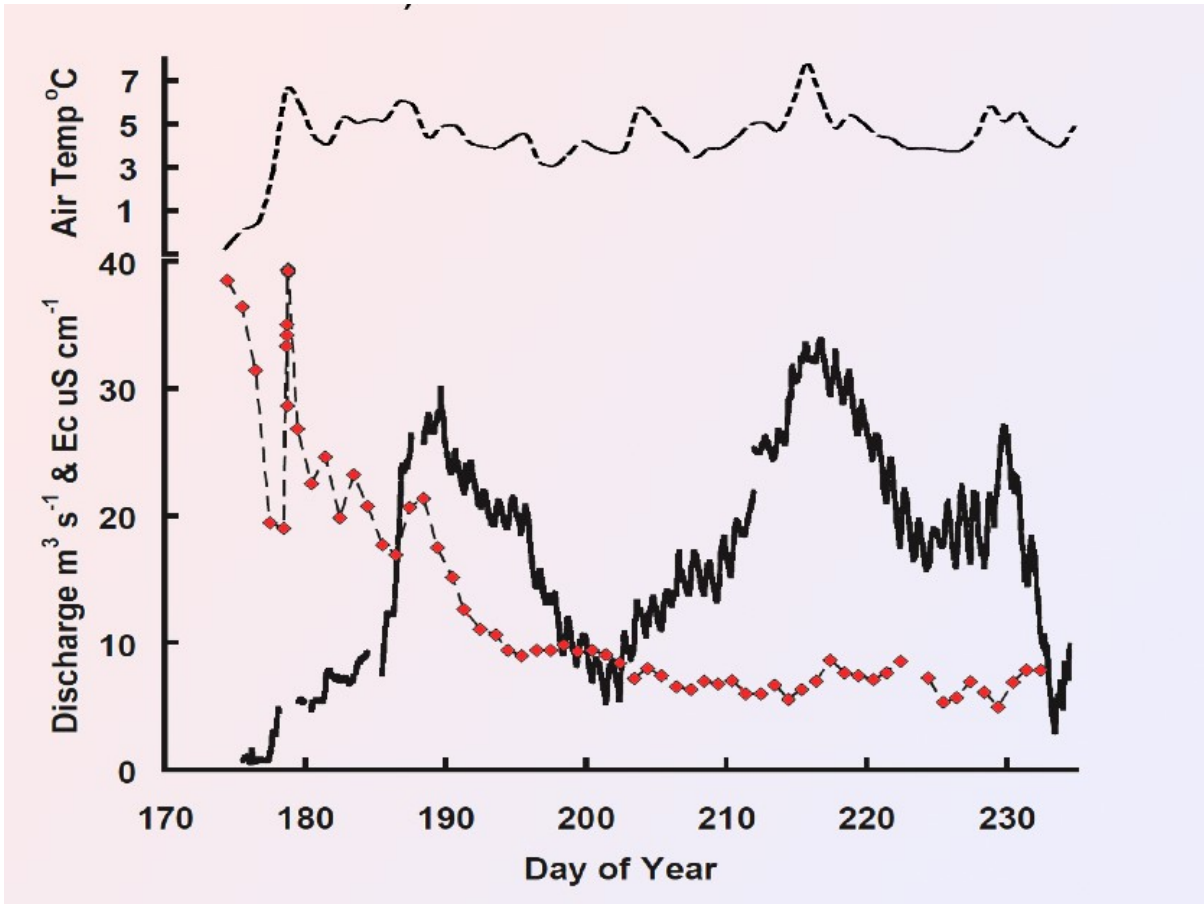

Figure 8.4 Variations in air temperature, discharge and conductivity from Bristol Glacier, Greenland, in 1999 (unpublished data, modified from Skidmore and Tranter).

The outburst finally came over the next couple of days. It was much slower and more sustained than we had had in our mind's eye. The interesting thing was that not only did the EC stay high, just like at Finsterwalderbreen, but that, in this case, it actually rose (Fig. 8.4). We were sure that we were onto a great story. The rest of the season was not so interesting, with the discharge rising and the conductivity falling to very low values. However, this just placed the hydro-fracture water and the outburst into sharper focus as defining an unusual, and potentially important, hydrochemical event. We speculated on the volume of water in store under the glacier, the nature of the overwinter drainage system and the factors giving rise to the outburst. You might wonder where the references are to this work, and why there are no further figures. A huge regret is that we have barely published any of the data.

8.4 The First Good Data for Ice Sheet Runoff

I always felt fortunate to have worked at Oceanography in Southampton and to have been around Denis Burton and Peter Statham's trace metal groups (Tappin *et al*., 1993). They had

given me an appreciation of the partitioning of trace metals between dissolved, colloidal and solid phases. David Hydes, at IOS Wormley, had also got me interested in how Al solubility seemed to be determined by the particulate compositions and concentrations in sea water (Hydes and Liss, 1977).

Mark and I wanted to know what happened to the Fe that arose from sulphide oxidation in subglacial environments. We figured that there should be a lot of colloidal Fe present in runoff or adsorbed onto suspended sediment, because Fe(III) is only sparingly soluble in oxygenated waters at the circum-neutral and higher pH typical of glacier runoff. Skid's naked mole rat strategy for producing contamination-free Fe concentrations in an otherwise dusty environment paid off handsomely. Marine scientists had long known that total dissolved metal concentrations in samples filtered through 0.4 μm filters produced, frankly, wacky results, giving concentrations of species such as dissolved Fe and Al that were supersaturated. Peter and David had drilled into me that supersaturated solutions were probably nonsense, and more likely artefacts of sampling and processing. They noted that filtering through 0.02 μm filters gave saturated solutions, and that it was colloids that passed through 0.4 μm filters, but were trapped by 0.02 μm filters, that were the cause of the apparently supersaturated concentrations. Mark took this idea and applied it to glacial meltwaters, step filtering his solutions (Fig. 8.5). It came up trumps. Solutions filtered through 0.02 μm filters were saturated with Fe(III), given the pH of the meltwater. This made perfect sense, given the ubiquitous presence of Fe in most glacier bedrocks. The main variability in Fe came in the colloidal fraction, which was also the predominant 'apparently dissolved' Fe phase. We used the mean concentrations of truly dissolved and colloidal Fe to produce estimates of fluxes of potentially bioavailable Fe to the coastal waters around Greenland and Antarctica (Statham *et al*., 2008). It was now up to the oceanographers to decide what would be the fate of this material during mixing with sea water (Hopwood *et al*., 2014, 2015).

1999 was a pivotal year in my career. Greenland had left a big impression on me, and I felt that ice sheets were the places to work for both scientific and societal reasons. Berry Lyons had invited me to work in the McMurdo Dry Valleys of Antarctica at the start of the year, and I had the great fortune to have Andrew Fountain put me through my paces in the field. Visits to both Greenland and Antarctica inside six months led me to look for similarities, rather than differences in the ice weathering systems. Microbiologists have the principle that every microbe is everywhere (but the environment selects). It's a bit of a stretch to say that all glaciers behave in approximately the same manner, but the processes of glacial erosion and fine sediment generation occur at most glacier beds. It struck me that, given allowance for variations in scale, climate, water flow paths, and the types of sediment found beneath the ice sheet (Tranter and Wadham, 2014), glacial chemical weathering was likely to occur by

fundamentally similar processes beneath most ice masses, given the presence of water. The major ion chemistry we obtained in 1999 from both Bristol Glacier similar to that of Haut Glacier d'Arolla, consistent with this idea, and I promise Mark and the Greenland team that I will publish the data shortly to back up this assertion.

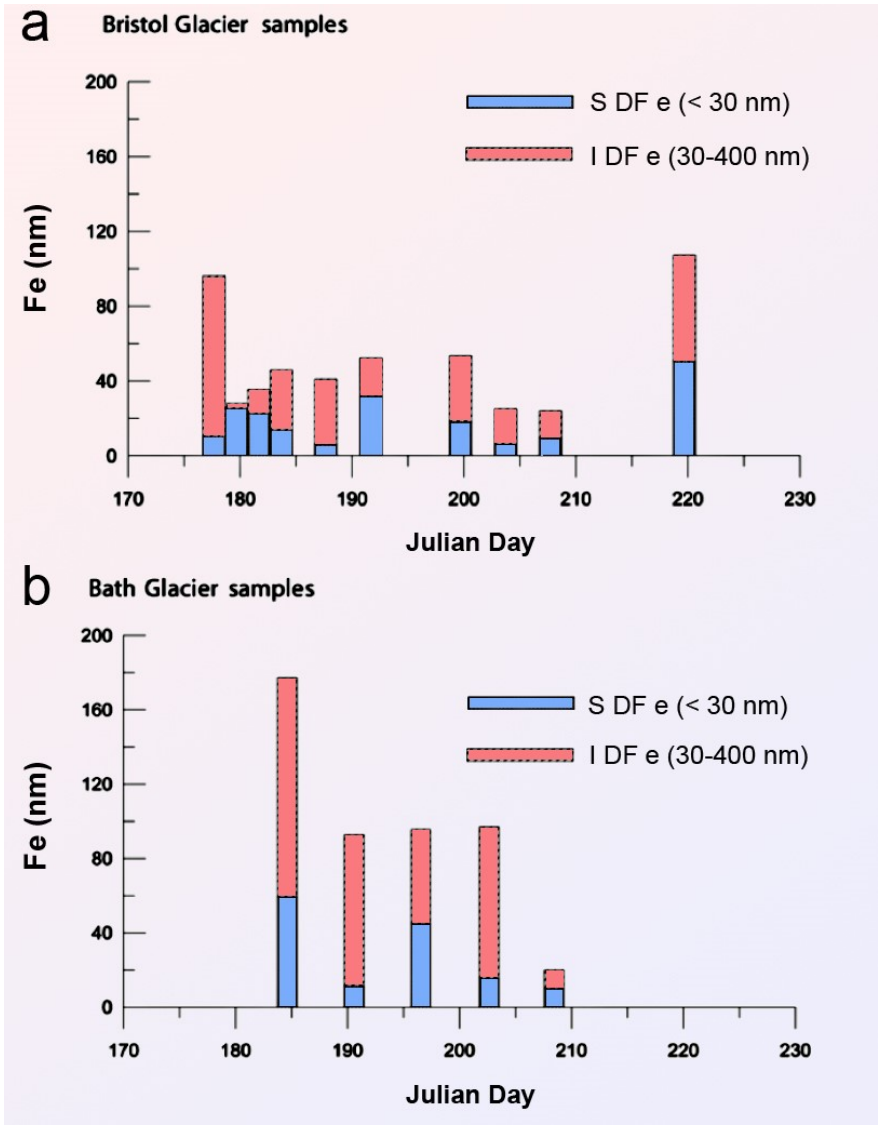

Figure 8.5 Concentrations of truly dissolved (<30 nM) amd colloidal (20-400 nM) Fe in runoff from Bristol Glacier, 1999 (modified from Statham *et al*., 2008).

8.5 Antarctica and the McMurdo Dry Valleys LTER (Long Term Ecological research)

The McMurdo LTER (Long Term Ecological Research) site is in Taylor Valley, Antarctica. It is known as the “Valley of the Dead” (Priscu, 1999), since seals and penguins that have the misfortune to crawl and walk into the valley, rather than walk across the sea ice at the bottom of the Valley into the ice-free waters of the Ross Sea, slowly dehydrate and die. Taylor Valley is dotted with the mummified carcasses of seals, and the occasional skeleton of an Adelie Penguin. The Code of Conduct for working in the Dry Valleys prevents one from interfering with or modifying the behaviour of the fauna, and it is heart breaking to most of us that we can observe, and not prevent, the slow demise of the penguins in particular. That said, Taylor Valley is an inspirational place for a water chemist. I can think of no other mosaic of terrestrial surface environments with such ranges of pH (~5 – 11), salinity (pristine snow to several times sea water) and Eh (oxic to anoxic) over length scales of several kilometres.

The LTER team is truly interdisciplinary (Moorhead *et al*., 1999), with biologists, microbiologists, chemists and physical scientists working closely together. My remit was to work with Andrew Fountain on the hydrology of the cold polar glaciers in the valley. Our base was at Lake Hoare, close to Canada Glacier. My first trip into Taylor Valley was by helicopter, and I could not see any water as we flew over the Dry Valley glaciers. The curious thing was that the glacier surfaces showed evidence of water flow, since valleys were carved into the sides of some of the glaciers, but they were completely frozen. The frozen valleys grew larger towards the margins of the glaciers, but they did not seem to carry any water. I wondered what I was going to spend three weeks studying.

Andrew was very patient with me. We have similar senses of humour, even when the joke is on us. He teased me about having little belief that melt could be produced from ice with a temperature of ~-20 ^{o}C and at air temperatures that were several degrees below zero. I just didn’t get the joke. We flew by helicopter to Taylor Glacier, at the head of Taylor Valley, which was higher, colder and windier than the glaciers nearer the valley base. This seemed the most stupid of places to search for liquid water. I looked around the site where we were dropped off and could see a stream channel that was frozen solid. Andrew threw me an ice corer and said “*drill – you’ll find water at depth*”. Frankly, I thought he was nuts. I thought it was a joke, but played along. I found nothing but ice for the first 20 cm, but then drilled into a cavity filled with water……. I still remember the feeling of being totally perplexed. The ice had an EC of ~1 µS cm^{-1}, and the water at depth had an EC of ~25 µS cm^{-1}. How did the water get there and how was the solute generated? I was hook, line and stinker taken with cold glacier hydrochemistry.

8.6 Falling in Scientific Love with Cryoconite Holes

Melt water is formed from the very cold ice, despite sub-freezing air temperatures, by the solar heating of debris that typically lies about 20-30 cm beneath the ice surface (Tranter *et al*., 2010; Bagshaw *et al*., 2013). Enough sunlight can penetrate to this depth to warm the dark debris sufficiently to produce meltwater from the surrounding ice. The water production there is a kinetic phenomenon. Heat energy accumulates in debris, ultimately producing melt water, because the ice conducts heat poorly. The water freezes if the solar radiation diminishes, for example on overcast days, and melt water is produced and the debris melts further into the ice if solar radiation continues. The debris contains inorganic minerals, and these can dissolve partially into the melt water.

The resulting solute is retained in the water as it freezes, since most common cations and anions do not fit well into the growing ice crystals. Hence, over time, the waters become more concentrated in solute than the ice they are melting from and into (Bagshaw *et al*., 2007). The morphology and evolution of the sub-surface, debris-floored water flow paths are beyond the scope of this chapter (Bagshaw *et al*., 2010; Tranter *et al*., 2010), but an element of this drainage system, cryoconite holes, really caught my imagination. Cryoconite holes are debris-floored depressions containing water that are found on glacier surfaces worldwide. Those in the Dry Valleys are frozen and ice topped for much of the short melt season, and can be thought of as goldfish bowls frozen into the ice surface. About half of those on Canada Glacier seemed to be connected to the sub-surface drainage system, and about half were isolated from it. Waters in connected holes were more dilute, while those in isolated holes could be quite concentrated in solutes. The debris in the floor of the cryoconite holes was home to a range of autotrophic microbes (which are organic carbon forming, rather like plants), primarily robust cyanobacteria. It also contained microbes that are decomposers, known as heterotrophs. Net photosynthesis in the closed cryoconite holes produced O_2 concentrations of up to 160 % saturation, and a pH of almost 11 (Tranter *et al*., 2004). This is an exceptionally high pH for a pristine water (Fig. 8.6). To me, they were the “light and surface” equivalent of the “dark” biogeochemical weathering systems at the glacier bed. John Priscu had written a paper on life in the frozen-topped lakes of the Dry Valleys (Priscu *et al*., 1998), and noted that wherever there was water near the Earth’s surface, there was life. I bought into this, since we had found life everywhere we had sampled water in glaciers to date.

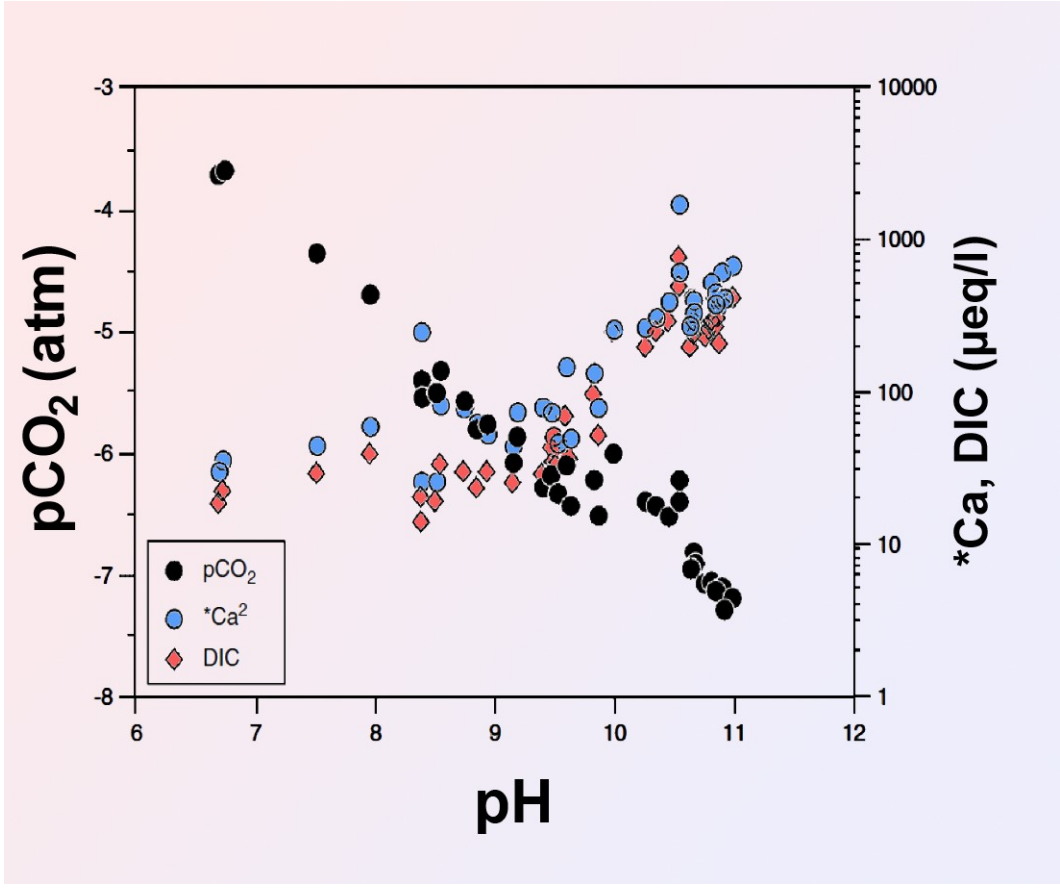

Figure 8.6 The Dissolved Inorganic Carbon (DIC) and Ca^{2+} concentrations, and partial pressure of carbon dioxide in waters entombed in cryoconite holes in the surface ice of Canada Glacier, Antarctica (modified from Tranter *et al*., 2004).

8.7 Antarctic Subglacial Lakes

I was fortunate that, *en route* to the Dry Valleys, I had a little time on my hands due to a bad bronchial infection, which left me holed up in the main science base, McMurdo, with the "grunge". The doctors would not let me into the field until I had responded to the antibiotics I had been prescribed. I picked up the latest edition of *Science*, and read a trio of papers concerned with the interpretation of the microbiology (Karl *et al*., 1999; Priscu *et al*., 1999) and geochemistry (Jouzel *et al*., 1999) of accretion ice recovered from the bottom of the Vostok Ice Core (Jouzel *et al*., 1997). The accretion ice was believed to be formed from waters freezing out of subglacial Lake Vostok. The papers were very, very interesting, since they provided evidence that there was life beneath the centre of east Antarctica, beneath almost 4 km of ice. The ice chemistry also grabbed my attention. I had a hard time understanding how the water isotopes married into the dynamics of the ice movement across the lake. The isotope variations were explained by the melting and freezing of a single mass of water and ice, and

yet water was continually being formed from the partial melting of ice flowing across the lake over the northern sector of the lake, and new ice froze and was carried out of the lake water in the southern sector – the ice flow across the lake brought in new basal ice to melt and carried away accretion ice frozen from the lake water. The lake seemed to be more of a steady state system than a single body of water that partially melted and froze.

These types of systems have very different water isotope variations. The heavier isotopes of oxygen and hydrogen concentrate or fractionate into the freezing ice, and so I felt that the water isotope concentration of the lake waters must be depleted in the heavier isotopes (Royston-Bishop *et al*., 2004). I discussed this with Berry Lyons, not realising that he was an author on John Priscu's microbiology paper (Priscu *et al*., 1999). We had similar views, and subsequent conversations led me to become more and more interested in subglacial lakes. It was around this time that Martin Siegert moved to Bristol, along with Julian Dowdeswell and Giles Brown, from Aberystwyth, when Julian founded the Bristol Glaciology Centre. Subglacial lakes were central to Martin Siegert's research (Siegert, 2001). We chatted about Blood Falls in Taylor Valley, where hyper-saline waters rich in Fe(II) were discharging periodically from the bed, turning bright orange as the Fe(II) oxidised to Fe(III) (Mikucki *et al*., 2009). I felt that this showed that microbial life existed beneath at least the outlet glaciers of Antarctica. The waters must have become anoxic because of oxidation of sulphides or organic matter, which Martin writes about below. John Priscu's paper (Priscu *et al*., 1998) noted that wherever there was water near the Earth's surface, there was life. Why not beneath ice sheets in subglacial lakes? I became convinced that microbes would be found in subglacial lakes, and Martin Siegert did too (Siegert *et al*., 2001).

The next few years were very productive times for the discipline. Jemma and Pete Nienow teamed up to conduct ground breaking work at Leverett Glacier on Greenland (Bartholomew *et al*., 2010). Skids returned to the States and worked on subglacial lakes, and ice stream and glacier bed biogeochemistry (Skidmore *et al*., 2010). Rob Raiswell became convinced that ice bergs could fertilise the Southern Ocean, and pounds away on that theme even today (Raiswell *et al*., 2008, 2016). I fell further in scientific love with the Dry Valleys, cryoconite holes and subglacial lakes, which lead me to work closely with Andrew, Berry, John, and Martin Siegert. There were more big issues and great colleagues to work with, but, as enjoyable as it was, it felt very uncomfortable to be spread so thin. Jemma very generously kept my interest in the hydrology and hydrochemistry of the Greenland Ice Sheet *via* a series of talented post-grads, Emily O'Donnell (*née* Lawson) (O'Donnell *et al*., 2016) and Catie Butler. I kept my interest in Svalbard glaciers alive *via* Marek Stibal, a microbiologist and lover of cryoconite holes too (Stibal *et al*., 2008). Liz Bagshaw took on board the cryoconite holes in the Dry Valleys (Bagshaw *et al*., 2007), and then the Bristol Glaciology Centre appointed

Alex Anesio, the most enthusiastic and upbeat colleague I have known. Alex is a very talented microbiologist, and soon got funding for work in Svalbard and Greenland to look at microbial successions from cryoconite holes to glacier forefields (Anesio and Laybourn-Parry, 2012). He appointed Jon Telling (JT), Jemma's lab technician, who is not so much "can do", but more "already have" (Telling *et al*., 2014). Jemma became very interested in nutrient fluxes from ice sheets (Wadham *et al*., 2016), and appointed a Masters student that JT and I had worked with in Svalbard on Alex's project. Jon Hawkings is driven (Hawkings *et al*., 2016), and a great guy to boot. He romped through his Ph.D. and into post-doctoral positions. These folks have been a pleasure and a privilege to work with, and have kept me on my scientific toes as I progress towards senility. I'll let Martin tell you more about the search for, and utility of, organic matter in subglacial environments.

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9. TOWARDS THE ORGANIC GEOCHEMISTRY OF GLACIERS (MS)

9.1 Introduction

When we first confirmed the existence of microbes in subglacial environments at Arolla, we started to think about how these microbial populations might be sustained at glacier beds – and about whether microbes might also be found in supraglacial and englacial settings and how the challenges to life in those environments might differ from those that would be encountered at the glacier bed. The work subsequently done in my group in Alberta by Mark Skidmore and Maya Bhatia was directed at some of these issues, but there was much that had not been touched. Thinking that oxidation of organic matter could be a significant source of carbon dioxide (and hence protons) for subglacial waters, we started to pay attention to whether and where organic matter could be found in these systems, and to the forms in which it occurred.

Some of the obvious advantages of the subglacial environment for microbes were a stable temperature regime, the presence of water (a source of nutrients) wherever the ice was at the pressure melting point, and the continuous renewal of the supply of nutrients, dissolved gases, and particulates to the subglacial system by a combination of glacial erosion, basal melting, and the seasonal transmission of surface meltwaters to the glacier bed. We recognised that inputs of organic particulates might be important for sustaining the subglacial ecosystem because they would provide a substrate for heterotrophic respiration (and thus a potential source of greenhouse gases – a thought that had us contemplating the notion of a "subglacial composter"!).

We knew that organic matter was deposited onto glacier surfaces from the atmosphere, and that algae grew on glacier surfaces, so the glacier surface was an obvious potential source of organic material for the subglacial ecosystem. However, given that the extent of glacial fluctuations over time in response to climate change and variability, it also seemed likely that there would be important subglacial sources of organic carbon from a variety of sources;

(i) Bedrock (such as shales - as was later suggested by Jemma Wadham on the basis of work on glaciers in in Svalbard (Wadham *et al*., 2004)),

(ii) Overridden soils (which Maya subsequently demonstrated at John Evans Glacier),

(iii) Permafrost (which could potentially thaw out over time when confined beneath a glacier),

(iv) Glacially-overridden plant material and soil carbon, and marine clathrate hydrates beneath the West Antarctic Ice Sheet (an idea subsequently developed by Jemma Wadham and others).

Needless to say, recognising the potential importance of organic carbon to subglacial microbial ecosystems was one thing - demonstrating it took us a while. As usual, it happened by a very roundabout route.

9.2 Organic Contaminants in Glaciers

Sometime in the late 1990's, David Schindler approached me with a question about some of the lakes in the upper reaches of the Bow River Basin in Banff National Park, Alberta. David Donald, from Environment Canada, had conducted a survey of Chlorobornane levels in water, sediment, and fish from 13 lakes along a transect from the Boreal Plain in Alberta, into the montane and subalpine ecozones of the Rocky Mountains (Donald *et al*., 1998). Five of these lakes had previously been treated with toxaphene in the period 1958-1962. However, the highest concentrations in fish from the lakes occurred in glacially-fed Bow Lake, which had no record of toxaphene usage. David Schindler wondered if I had any idea why that might be the case.

I was aware of some work by sedimentologist Norman Smith, who had investigated processes of sedimentation in four glacially-fed lakes in the upper Bow catchment, including Bow Lake (Smith *et al*., 1982). One of his findings was that most of the sedimentation of glacial

rock flour in Bow Lake occurred in the form of faecal pellets of pelagic copepods – which were presumably feeding on the suspended rock flour. My immediate, and incorrect, thought was that if organic contaminants were being released from a reservoir in the Bow Glacier (Fig. 9.1), and if they became bound in some way to the fine grained rock flour, then maybe they were being absorbed by the copepods that were feeding on the rock flour, and then bio-accumulated up the food chain in the lake. This would not happen in non-glacial lakes because of the lack of rock flour in the water column.

Figure 9.1 Bow Lake with Bow Glacier in the background.

Unbeknown to me, David Donald had already shown that there was such a reservoir of organochlorine pesticides in glacier ice at Snow Dome on the Columbia Icefield (Donald *et al.*, 1999). Deposition of these compounds at Snow Dome had peaked in the 1980's, a decade or more after they had been banned and were no longer used in North America (Fig. 9.2). This delay was attributed to the time required to transport these volatile compounds *via* the atmosphere from areas where they were used to areas where they were removed from the atmosphere by the process of "cold condensation". Donald had suggested that the presence of this reservoir of pesticides in glaciers might mean that they would continue to be released into alpine and northern aquatic ecosystems for decades or even centuries. If he was correct, then a more likely explanation of the high POP (persistent organic pollutant) concentrations in Bow Lake copepods was that Bow Lake was the only lake sampled that had a glacial meltwater input. This argument was enough for David Schindler and me to obtain funding to pursue the idea. We were joined by Jules Blais as a post-doc and Melissa Lafreniere as a Ph.D student to work on the problem.

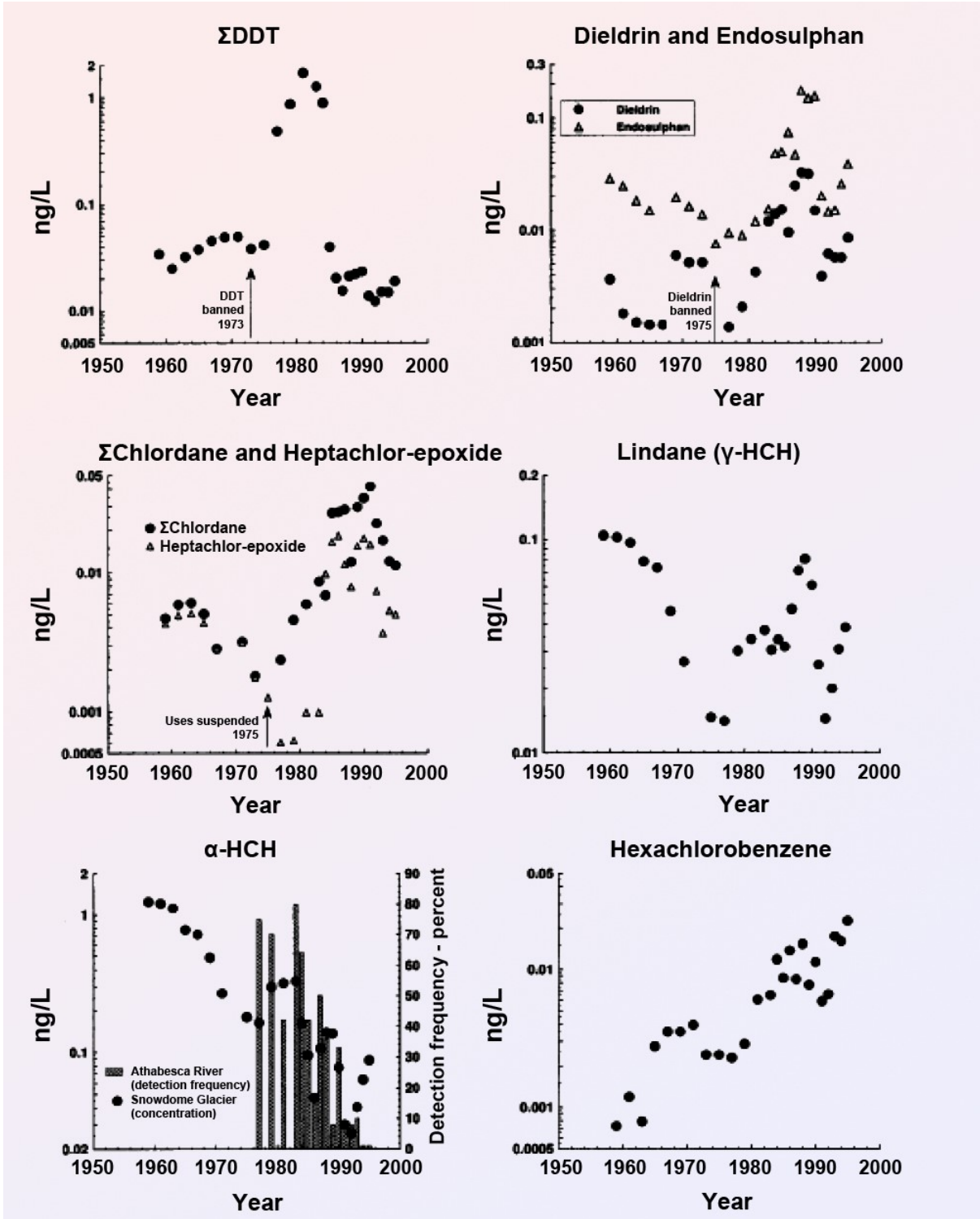

Figure 9.2 Concentration of organochlorine pesticides and isomers at Snow Dome Glacier, 1959-1995. All concentrations are smoothed with a 3 point moving average. Detection frequency for alpha-HCH is for a site on the Athabasca River 115 km downstream from Snow Dome (modified from Donald *et al*.,1999).

Jules began by making a detailed survey of the abundance of POPs in snow along an elevation gradient into the high alpine environment of the eastern slope of the Alberta Rocky Mountains. He found that depositional fluxes increased by a factor of between 10 and 100 between elevations of 770 and 3,100 m (Blais *et al.*, 1998) (Fig. 9.3). This made sense since these compounds are both volatile (*i.e.* they tend to partition into the vapour phase at warm temperatures) and cold-condensing (*i.e.* they condense out of the vapour phase at low temperatures). This "cold condensation" effect had previously been proposed to explain changes in depositional fluxes of POPs with respect to latitude, but not with respect to altitude.

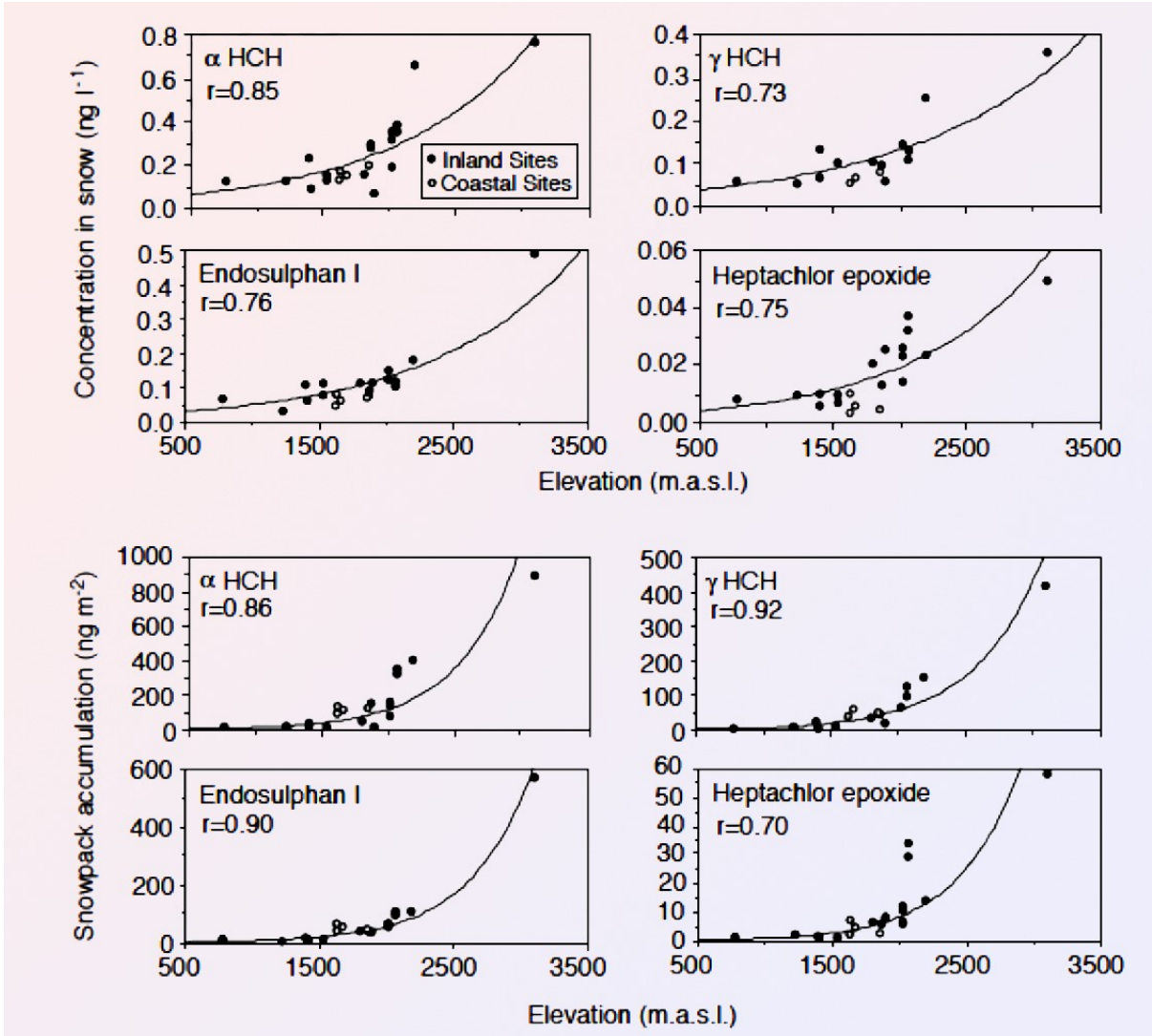

Figure 9.3 Organochlorine concentrations in snow and snowpack inventories for selected organochlorines as a function of elevation in western Canada. All replicates are shown as separate points. Increased enrichment in concentration with elevation was observed for more volatile compounds. Open circles represent samples taken near the coast of British Columbia while filled circles represent samples collected at sites further inland (modified from Blais *et al.*, 1998).

When we sampled stream waters to establish concentrations of organochlorine compounds in them, we found relatively high concentrations in the glacial melt stream draining from Bow Glacier and much lower concentrations both in a stream that drained a glacier-free alpine catchment, and in the snowmelt-fed Bow River, which also has its headwaters in a sub-alpine catchment (Fig. 9.4; Blais *et al*., 2001). This strongly suggested that there was something unique about glacial runoff that made it a more important vector for the export of organochlorine compounds than runoff in streams fed largely by extra-glacial snowmelt. Completing the organochlorine budget for Bow Lake, Jules found that gas absorption from the atmosphere was also a significant means of transferring organochlorine compounds into the lake, while volatilisation, stream outflow, and sedimentation were the main pathways by which they were removed.

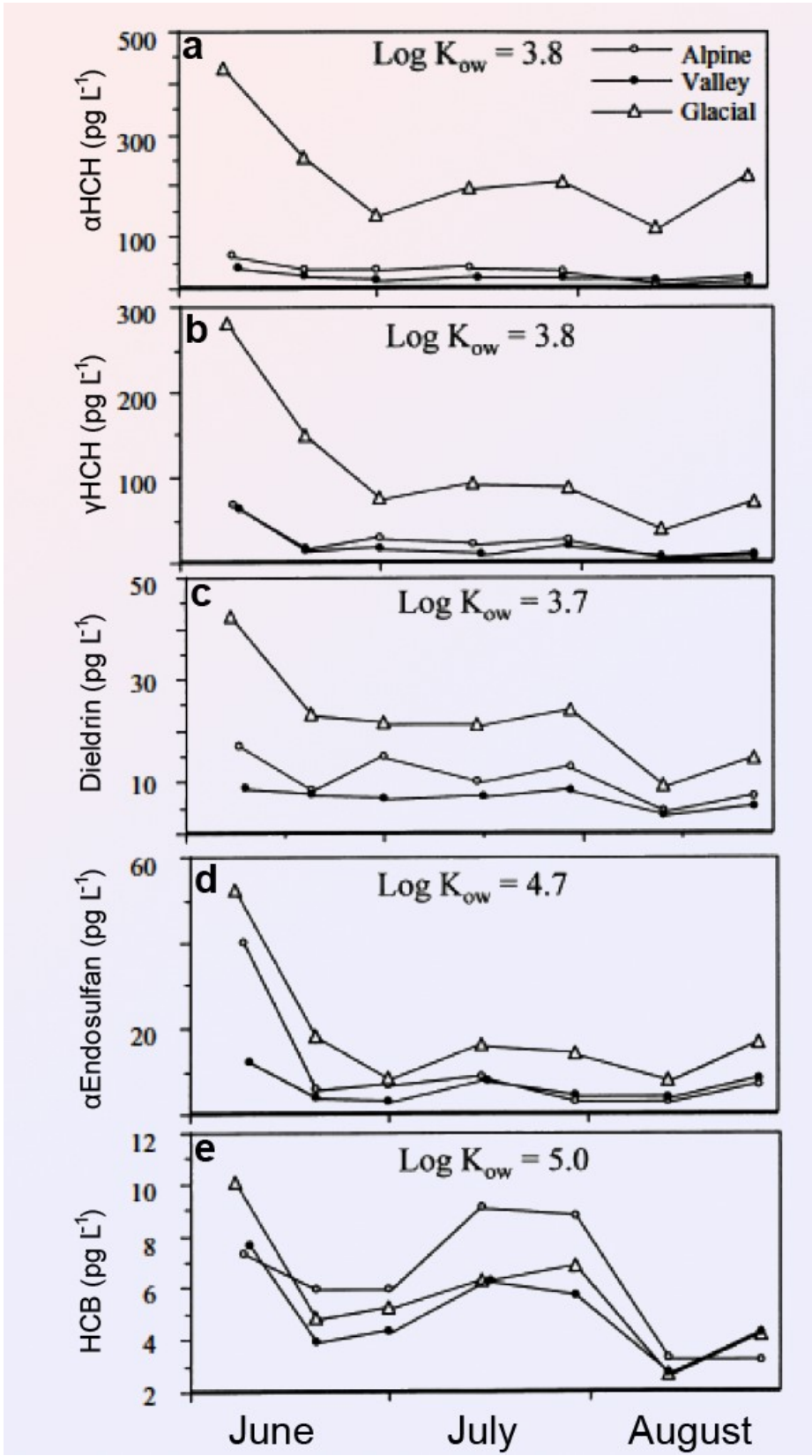

Figure 9.4 Concentrations for alphaHCH, gammaHCH, Dieldrin, alpha Endosulfan, and Hexachlorobenzene (HCB) in the three streams flowing into Bow Lake during the summer of 1997 (modified from Blais *et al.*, 2001).

Overall, melting glaciers supplied 50 to 97 % of the input of organochlorine compounds to Bow Lake, while contributing 73 % of the water input. An unusually high fraction of the POPs was transported in solution, suggesting that these compounds did not readily adsorb to suspended sediment in the glacial stream, probably because of its low organic matter content. We thought the importance of the glacial input reflected the fact that the flow routing of glacier runoff limited contact between water and organic-rich catchment soils, leaving the organochlorine compounds in the dissolved phase. Thus, the prevalence of inputs of organochlorine compounds to the lake in the dissolved phase, coupled with the low concentrations of dissolved organic carbon (to which the organochlorine compounds might absorb) in both glacial meltwaters and glacier-fed lakes, might be important factors in explaining why concentrations of these compounds were elevated in fish and other aquatic biota that inhabit glacier-fed lakes (relative to fish and aquatic biota in snowmelt-fed lakes).

Having said that, we also suspected that the nature of the glacier drainage system at Bow Glacier might play a role. On the glacier surface, runoff quickly became channelised and the channels sank into crevasses above the glacier terminus. This minimised opportunities for the meltwater to interact with any organic matter that might be on the glacier surface. When it emerged from the Bow Glacier, the runoff entered a small proglacial lake with a single outlet stream. Water exited this lake and flowed through the proglacial area *via* the outlet stream, which was generally steep and rocky. The water therefore had little opportunity to interact with organic soils or vegetated surfaces before it entered Bow Lake. Hence it retained much of its POP load and delivered it to the lake, where POP concentrations were sufficiently high that POPs could enter the lake food chain by passive absorption across cell walls.

By contrast with this system, it seemed likely that the Bow River headwaters would transport relatively high levels of dissolved organic matter. Bow River headwater runoff is derived in a highly distributed manner from snowmelt and rainfall in a well-vegetated catchment where soils typically have a near surface organic horizon. This likely offers an effective means for removing POPs from runoff by sorption onto organic matter, explaining why POPs were largely absent from snowmelt runoff. By contrast, glacier runoff that is generated from melt of glacier ice or snow overlying that ice, or from rainfall which runs off over the glacier surface, has little opportunity to interact with OM, so POPs are likely to stay in solution.

Subsequent to our work, Christian Bogdal and others (Bogdal *et al*., 2009) conducted a similar study in the Swiss Alps, where they found that POP release from melting glaciers could largely account for the upward increase in POP concentrations in the sediments of a glacially-fed lake. These authors argued that climate warming was likely accelerating the release of POPs stored in glaciers into the broader environment, but showed, through modelling, that ~50 % of the POP load originally deposited on the glacier was still retained in the glacier. This suggested that continued climate warming would likely result in the release of that POP reservoir into the broader environment. In another related study, Geisz *et al*. (2008) reported that ratios of (p,p'-DDT + p,p'-DDE) in Adelie Penguins in the western Antarctic Peninsula have declined substantially since 1964, indicating that these birds are being exposed to sources of old, rather than new, ∑DDT. They suggested that glacial meltwater was the likely source of this old ∑DDT to Antarctic coastal seas (Geisz *et al*., 2008).

9.3 Organic Carbon in Glacial Runoff

One problem with our argument that the relatively high POP fluxes into Bow Lake *via* the glacial stream were, at least in part, due to the limited contact between waters flowing through that stream and soil organic matter during their transit from glacier to lake was that we had no direct evidence that this was the case. Melissa Lafreniere set out to tackle that problem by monitoring dissolved organic carbon (DOC) concentrations in both the glacial stream and the Bow River headwaters in the summers from 1998-2000 (Lafreniere and Sharp, 2004) (Fig. 9.5). Typically, runoff in the Bow River headwaters peaked in June and/or early July, while glacial runoff peaked from mid-July to mid/late August. This is consistent with snowmelt being the main runoff source in the Bow headwaters and melt of glacier ice (which follows removal of the overwinter snowpack on the glacier) being the main runoff source in the glacier-fed stream. Typically, DOC concentrations in the Bow headwaters peaked (at 1.5-2.0 ppm) in May or early June and decreased significantly (to 0.5 ppm or less) thereafter, indicative of a flush of DOC from catchment soils during spring snowmelt. Concentrations in the glacial stream peaked (at around 0.7 ppm) later (in mid to late June) and then stabilised at around 0.3-0.4 ppm.

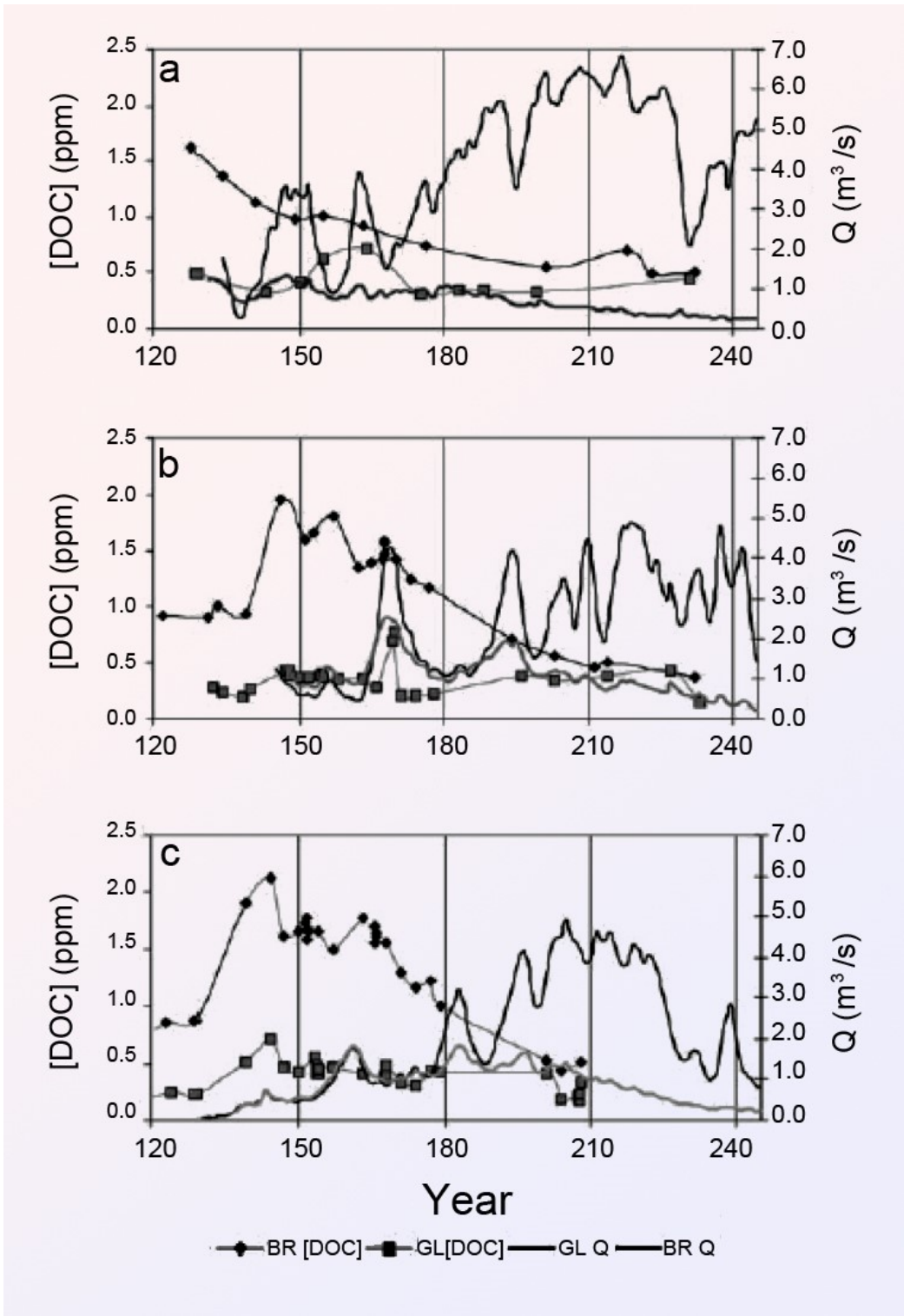

Figure 9.5 Stream DOC concentration (DOC) and discharge (Q) in the Bow River (BR) and glacial stream (GL) **(a)** from May to August 1998, **(b)** 1999, and **(c)** 2000 (modified from Lafreniere and Sharp, 2004).

These results seemed to support the idea that runoff from the glacial sub-catchment did indeed have less contact with soil organic matter than did snowmelt runoff. However, Melissa also wanted to determine whether runoff was coming into contact with different types of organic matter in the 2 sub-catchments, since it was possible that this might influence the properties of the DOC and the likelihood of POPs absorbing to it during transit through the different drainage systems. To address this issue, she turned to the emerging technique of measuring the spectrofluorescence of the Dissolved Organic Matter (DOM) (Donahue *et al*., 1998; McKnight *et al*., 2001). This involves exciting the sample with light emitted at a wavelength of 370 nm, and measuring the light emission from the sample at 1 nm intervals between 370 and 700 nm, and correcting the results with those from a sample blank (deionised water). She then characterised the DOM using three different indices derived from the resulting spectra: the Fluorescence Index (FI, the ratio of emission intensity at 450 nm to 500 nm for excitation at 370 nm; the peak intensity of fluorescence; and the wavelength of peak fluorescence). Previous work had suggested that the FI of mainly microbial DOM was ~1.9-2.0, while that of DOM from primarily terrestrial sources was ~1.4 (Donahue *et al*., 1998). The wavelength of peak fluorescence also varies with DOM provenance, the peak being at ~445 nm for microbial DOM and at 455 nm for DOM from soils and vegetation.

This approach proved to be successful, indicating that the DOM in the Bow River headwater streams was derived largely from soil and plant organic matter, which seemed to be flushed to the stream at the onset of snowmelt by shallow subsurface flow. DOM in runoff from snowmelt in ice-free areas of the Bow Glacier stream catchment had similar properties (especially during periods of summer rainfall), while that in the glacier melt stream was much more microbial in character (*i.e*. it consisted of the products of microbial metabolism or the decomposition of microbial biomass). Thus, the high concentrations of POPs in the glacial stream might reflect not just the low concentrations of DOM in the stream, but also the specific (microbial) origins of the DOM that was present. This suggested a difference in the degree to which the POPs would bind to different types of organic matter. The important point though, was that glacially-derived DOM had distinctive properties, relative to DOM found in most previously studied surface waters. This raised the question of how it might influence the suite of chemical processes active in glacial meltwaters.

9.4 Characterising Glacial Organic Matter – Fluorescence Methods

Joel Barker was an undergraduate student in the first class I taught after I moved to Alberta in 1993, and a member of the first field party to visit John Evans Glacier in 1994. After

finishing his undergraduate degree, he moved to the University of Western Ontario to work with Chris Smart on a project in groundwater hydrology for his M.Sc. After that, he came back to Alberta for his Ph.D. and he picked up where Melissa had left off on the DOM story. One of his goals was to look at DOM from a range of different glacial settings to see if variations in climate and glacier thermal regime were reflected in the properties of the DOM found both within glaciers and in the water draining from them. He chose to work on three glaciers in very different climatic settings – John Evans Glacier (in a cold dry Arctic setting), Victoria Upper Glacier in the McMurdo Dry Valleys, Antarctica (also cold and dry, but largely removed from likely sources of plant-derived OM), and Outre Glacier in the very maritime environment of northwest British Columbia (Barker *et al*., 2006). Joel's work in Antarctica was facilitated by a collaboration with Sean Fitzsimons in Otago. On the advice of Julia Foght, we also started to work with Ray Turner in Calgary to analyse the full fluorescence spectra of glacial DOM. Joel focused on how the location of emission peaks varied between samples and on how the intensity of emission varied with excitation wavelength – something that had not yet been done systematically on glacial DOM. Ray had a spectrofluorometer which, at that time, no-one at the University of Alberta did, and he was happy for us to use it.

In his first paper, Joel made a comparison of the abundance and fluorescence properties of DOM in supraglacial runoff, subglacial meltwater, glacier and basal ice at his three study glaciers. He found detectable amounts of organic carbon (0.06-46.6 ppm) in all the samples he analysed, though the fluorescence characteristics of the DOM varied between glaciers and sub-environments, and also over time in meltwater samples (Fig. 9.6). They were also quite different from those previously reported from other environments. He found that the fluorescence properties of DOM exiting the glaciers in meltwater runoff could differ from those of DOM in supraglacial meltwaters, and that there appeared to be sources of both microbial and terrestrial DOM in the subglacial environment. This was suggestive of active cycling of organic carbon at the glacier bed. There was also some evidence of variability in DOM properties and abundance within the ice of Victoria Upper Glacier. Tyrosine-like fluorescence was found ubiquitously in samples of both glacier ice and debris-rich basal ice, suggesting that *in situ* production was likely.

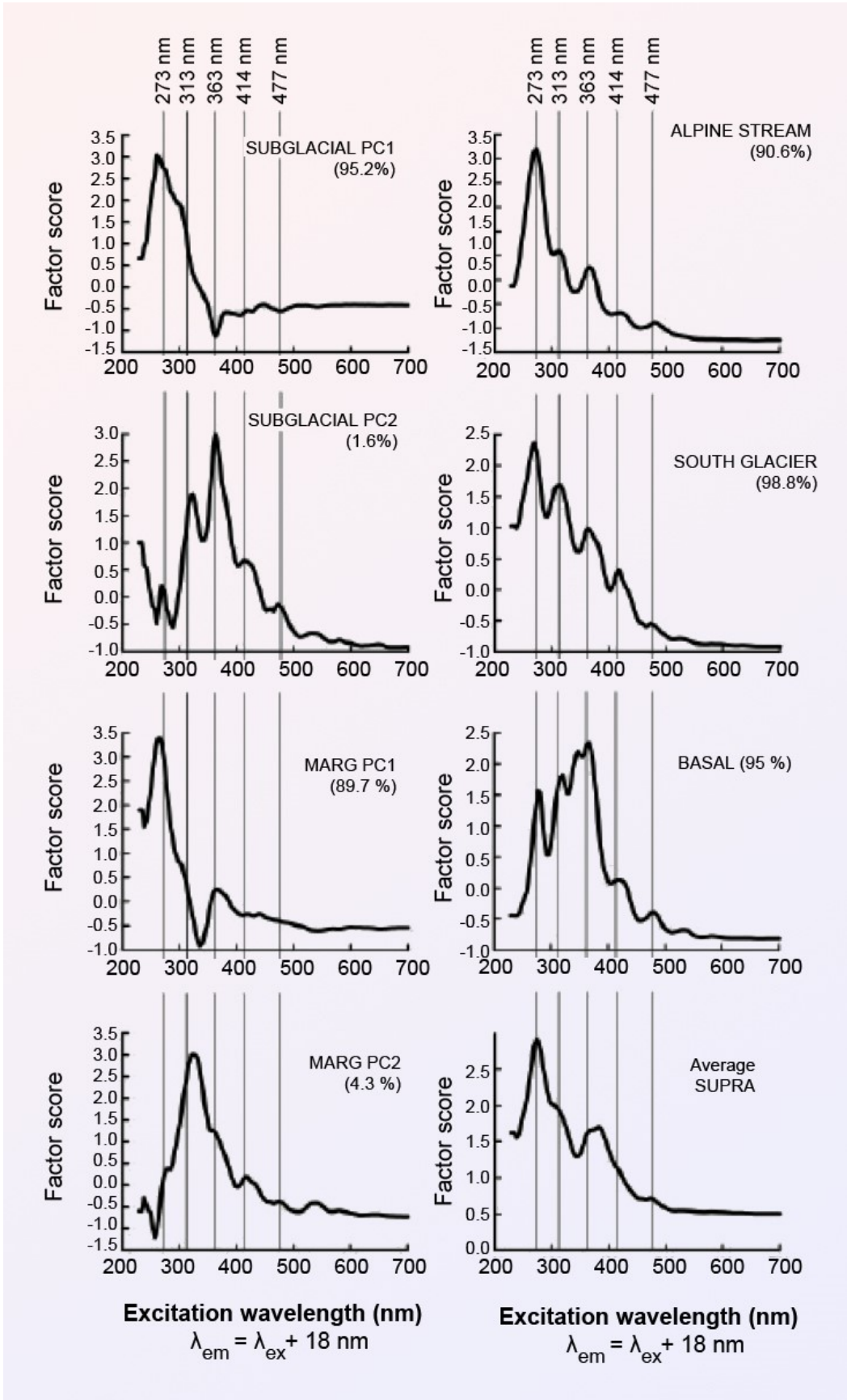

Figure 9.6 The spectral waveforms associated with the principal components (PC) of the fluorescence spectra of dissolved organic matter from different sub-environments at Outre

Glacier in the Coast Mountains of British Columbia. Spectra are from the subglacial, ice marginal (MARG), supraglacial (SUPRA), and alpine (non-glacial) streams, from debris-rich basal ice (BASAL), and from the stream draining nearby South Glacier. Sample size for SUPRA was too small to allow calculation of principal components, so the average spectrum is plotted. The subglacial and marginal stream samples each yield 2 PCs, while the others each yield only one (modified from Barker *et al*., 2009).

In a second paper, based on work at Outre Glacier, Joel analysed temporal variability in the fluorescence spectra of DOM exported from the glacier in meltwaters over the course of a melt season (Barker *et al*., 2009) (Fig. 9.6). He found that, over most of the melt season, the DOM was characterised by a single tyrosine-like fluorophore that was likely incorporated into runoff during snowmelt on the glacier surface. However, at high flows, a second, humic, DOM component was present in the runoff. The same component was also found in waters from a nearby non-glacial stream. Joel argued that it was derived from a glacially-overrun moss-covered soil environment. This component was mobilised during high flows when waters that were normally confined to a major subglacial drainage channel would flood areas of the glacier bed that were not usually well-connected to the channelised subglacial drainage system. A third DOM component that contained both humic and proteinaceous fluorophores was found in runoff during periods of warm air temperatures and was thought to be flushed from cryoconite holes on the glacier surface. Although the fluorescence spectroscopy approach provided only a rudimentary characterisation of the glacial DOM, Joel's results were enough to suggest that there could be value in trying to characterise the DOM with more sophisticated methods.

The next step forward in this work came with a change in the way we characterised the fluorescence spectra of organic matter in glacial systems, and it was Ashley Dubnick, then an undergraduate student, who did this work for her Bachelor's thesis. Ashley compiled a set of 80 ice and meltwater samples from seven glaciers – 4 in Antarctica, 2 in Arctic Canada and 1 in Arctic Norway. These glaciers ranged from cold-based to temperate in thermal regime, and from maritime to continental in climatic regime, and they also differed in terms of likely sediment sources, which included aeolian sediments, glaciolacustrine sediments, soils, and vegetated land surfaces. Marine aerosol may also have been a potential OM source at three of the sites. Samples included various types of basal sediment-rich ice, glacier ice, snow, and meltwaters from the glacier surface, glacier bed, and proglacial streams and lakes.

Ashley analysed the samples in a consistent manner, using spectrofluorescence measurements to construct *excitation-emission matrices* (EEMs). Here, fluorescence scans are carried out to measure the light emitted over a range of wavelengths in response to excitation at a series of known wavelengths. The EEMs are essentially a contour map of fluorophore intensity for each sample. Each fluorophore represents the presence of a DOM fraction that can be characterised in general terms such as "humic-like", "fulvic-like", "tryptophan-like" or "tyrosine-like". Samples can then be compared and classified on the basis of the relative abundance of these fluorophores in the sample (Dubnick *et al*., 2010).

Ashley applied the technique of Parallel Factor Analysis (PARAFAC) to each sample to reduce the dimensions of the fluorescence dataset, and identified five significant fractions of DOM in the dataset as a whole (Fig. 9.7). Together these accounted for over 98 % of the variance in the dataset. Each fraction plots in a different region of the emission-excitation matrix for the sample. Comparison with previous work from other environments suggested that one of these fractions was "humic-like", while the other four were "protein-like". The four protein-like components accounted for 89 % of the variance in the dataset, while the humic-like one accounted for 11 %. Proteinaceous DOM accounted for at least 70 % of the modelled fluorescence in each sample, suggesting a significant microbial source of DOM in these systems. This was consistent with the results of previous work by Melissa Lafreniere and Joel Barker, and of an independent study of 11 Alaskan watersheds by Eran Hood and others (Hood *et al*., 2009) which had found that proteinaceous DOM was more abundant in runoff from glaciated watersheds than in runoff from watersheds with little or no glacier cover. This strongly suggested that DOM in glacial runoff is substantially different in composition from DOM in marine, estuarine and fluvial environments (in which at least half of the modelled fluorescence is humic-like). Ashley found that samples did not cluster together on the basis of either the glacier or the geographic region from which they were obtained, or on the basis of the sub-environment from which they came. She argued that these results strongly suggested the ubiquitous occurrence of a small number of relatively unique DOM fractions that were likely microbial in origin. She did, however, identify 4 distinct clusters of samples that were distinguished by differences in the relative proportions of humic- and protein-like fluorescence that they contained. Each cluster included samples from every glacier system sampled.

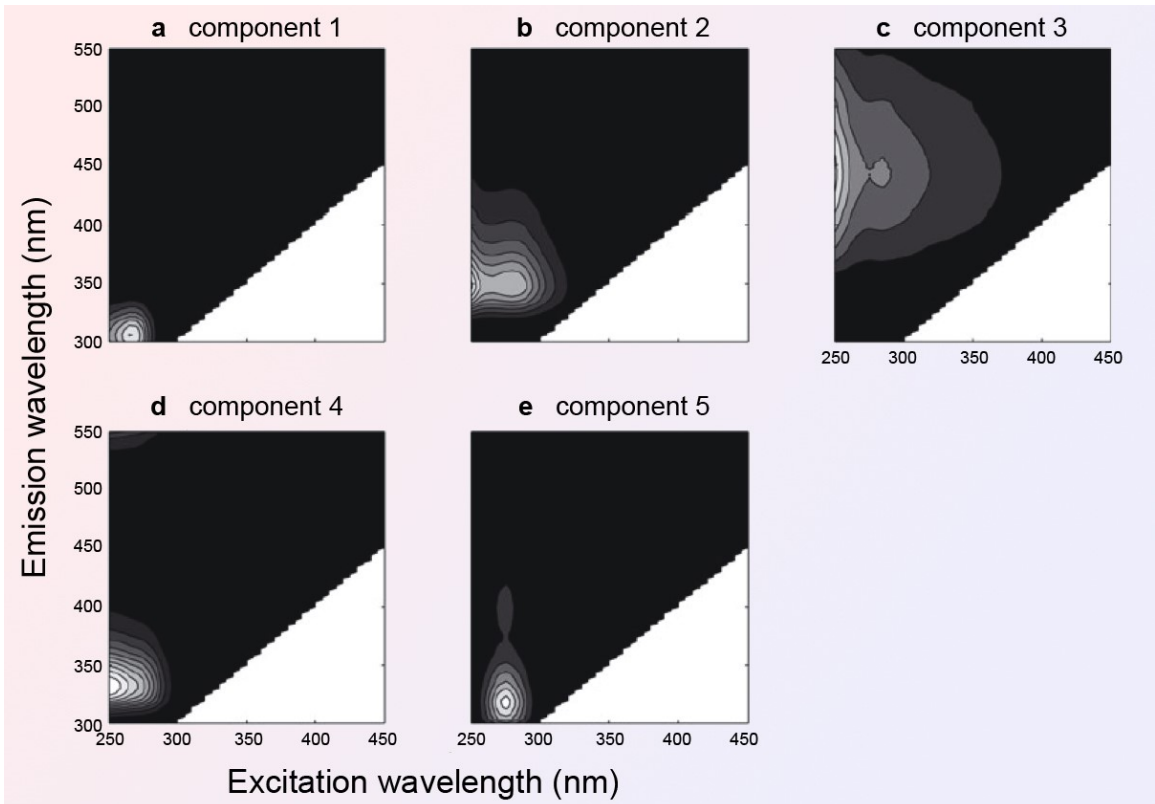

Figure 9.7 Principal Components of Emission Excitation Matrices (EEMs) computed using the PARAFAC technique for a suite of 80 ice and meltwater samples from supraglacial, englacial, subglacial, and proglacial environments at 7 glaciers. Components 1, 2, 4 and 5 are dominated by protein-like fluorophores suggestive of *in situ* microbial production, while Component 3 has a more humic character (from Dubnick *et al.*, 2010).

Snow and glacier ice samples contained similar DOM types, which probably suggests an atmospheric source (such as wind-blown material or snow-nucleating bacteria) for some DOM fractions. Samples of basal ice and meltwater turned up in every cluster, but meltwater samples had higher ratios of humic-like to protein-like fluorescence than snow and ice samples. Whether this was due to addition of humic DOM to meltwater as it passed through the glacier drainage system, or to preferential removal of protein-like DOM from meltwater (by a process such as heterotrophy or humification) was not determined. So, we were now relatively certain that glaciers contained DOM with characteristics that were quite different from those of the DOM fractions that dominated most other types of natural water, and that this DOM was microbial in character. However we didn't have much of an idea of what specific compounds were present in, or absent from, glacial systems.

9.5 Characterising Glacial Organic Matter – NMR and Biomarker Methods

To address this issue, we clearly needed to find a more sophisticated way to characterise the DOM. For this, we turned to Myrna and Andre Simpson at the University of Toronto and their student, Brent Pautler. Myrna was a graduate student in Soil Science at the University of Alberta when I first moved there, and was a friend of Mark Skidmore, so we had met a few times. She had subsequently honed her skills at Ohio State University where she had teamed up with Andre. They had set up a Centre for Environmental Nuclear Magnetic Resonance Studies on the Scarborough Campus in Toronto and were doing really novel and interesting work on organic matter characterisation. Fortunately, they were interested in exploring the character of organic matter in glaciers and Ashley and I started to send them samples to see what they could find.

The first samples we analysed came from the 50 m high terminal ice cliff of Victoria Upper Glacier in the McMurdo Dry Valleys of Antarctica, which I had visited with Sean Fitzsimons of the University of Otago. Sean was working on the origins of the basal ice in the cold-based glaciers in this region and had become an expert in glacier tunnelling. The 50 m high ice cliff that we sampled (by cutting blocks with a chain saw) consisted of glacier ice overlying ~15 m of debris-bearing basal ice that was obviously affected by the glacier's interaction with its bed, with a narrow transition zone between these two ice types. Dissolved Organic Carbon concentrations averaged 8 mg L^{-1} in the glacier ice, 3 mg L^{-1} in the basal ice and 12 mg L^{-1} in the transition zone. These blocks were subsequently sub-sampled in a sterile cold room using a clean bandsaw after removal of a 3 cm thick layer of ice from all surfaces of the block to minimise contamination from the sampling process. They were then analysed in Toronto (at natural abundance levels) using the new technique of SPR-W5-WATERGATE ^{1}H NMR Spectroscopy (Pautler *et al*., 2011).

The results (Fig. 9.8) showed that the main components of the DOM in each ice type were lactic and formic acid, free amino acids, and a mixture of simple sugars and amino sugars. Concentrations varied between ice types. Free amino acid and amino sugar monomer components of peptidoglycan were found in the ice. These are normally considered to be biologically labile or fast cycling in other environments, suggesting that they form as a result of in-ice microbial activity, likely from more refractory precursor forms of organic matter. The presence in the ice of biomolecules such as lactic and pyruvic acid that are associated with bacterial energy cycles, and metabolic by-products such as MeOH and small organic acids, also suggested *in situ* microbial metabolism. This was by and large consistent with what we had inferred from our previous work based on spectrofluorescence measurements, and suggested that release, by ice melt, of biologically labile constituents of OM could be a

stimulus to carbon cycling in proglacial aquatic systems – as previously suggested by Eran Hood and others (2009).

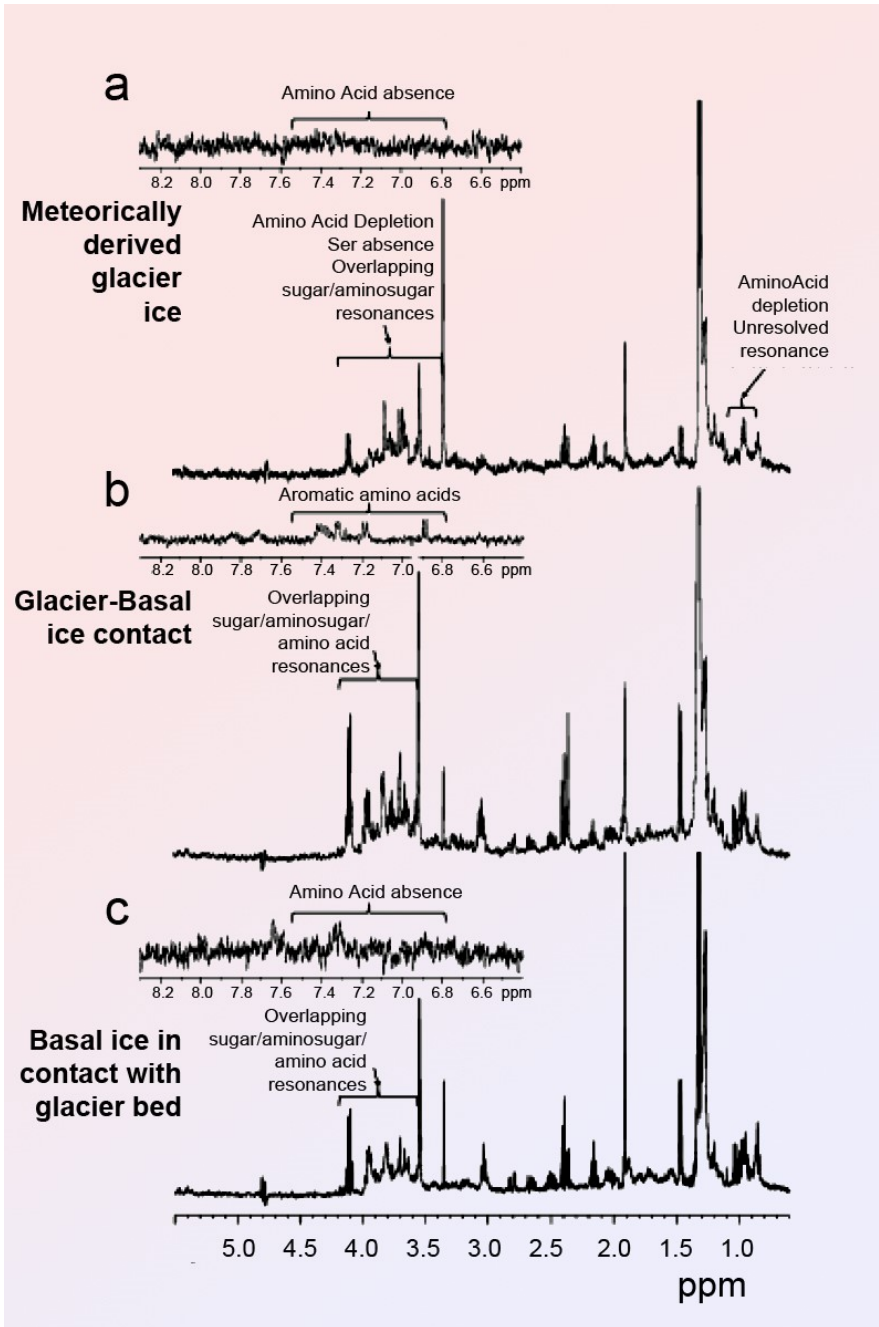

Figure 9.8 The first SPR-W5-Watergate ^{1}H NMR Spectra from glacial ice. Samples from Victoria Upper Glacier, Antarctica. **(a)** Glacier Ice, **(b)** Glacier Ice/Basal Ice contact, and **(c)** Basal Ice in contact with the glacier bed (modified from Pautler *et al*., 2011).

This initial study was of particular importance because it demonstrated that we could effectively characterise the composition of DOM from glacier ice at natural abundance levels.

The results we had obtained were consistent with what we had inferred from our earlier spectrofluorescence work, but we had yet to make a direct comparison of the two methods using results obtained from exactly the same samples. That was the next step in our collaboration with the Simpson group (Pautler *et al*., 2012). For this work we analysed samples from glacier ice (9 samples) and basal ice (4 samples) obtained from three glaciers in the McMurdo Dry Valleys (Victoria Upper Glacier, Clark Glacier, and Joyce Glacier) and two glaciers in the Canadian Arctic (White Glacier and John Evans Glacier). We analysed the spectrofluorescence data using the PARAFAC (Parallel Factor Analysis) method.

The DOM components identified by PARAFAC were all mainly proteinaceous in character (a characteristic that we had previously associated with a microbial origin), although there was also a terrestrial component. This was consistent with the results of Joel and Ashley's previous work. The ^{1}H NMR spectroscopy revealed a mixture of small molecules that were probably associated with native microbes, but did not detect the terrestrial OM contribution inferred from the spectrofluorescence analyses, (suggesting that this component was present at very low abundance levels). It did, however detect the presence of levoglucosan (which forms by the pyrolytic breakdown of cellulose during biomass burning) in samples of glacier ice from the Arctic. This presumably indicates episodic fallout from biomass burning plumes. However, DOM from basal ice in both Arctic and Antarctic glaciers was very similar to that in glacier ice from the same locations. This suggests that any soil organic matter in basal ice was present as either particulate OM or coatings on mineral grains, and not as DOM. Having said that, the ^{1}H NMR spectral line width in the basal ice samples was broader than that in the glacier samples, which might indicate biological degradation of DOM within the basal ice.

9.6 DOM on Glacier Surfaces

Thus far, our work with the Simpson group had focused on DOM in glacier ice and basal ice and paid no attention to DOM on the glacier surface, where it was known that there was often a unique material, known as cryoconite, a mixture of fine grained mineral material, organic matter and living organisms. Characterising this material, identifying its sources, and assessing the extent of OM degradation and microbial activity using samples from 4 glaciers in the Arctic (John Evans Glacier), Antarctic (Joyce and Garwood Glaciers) and Greenland (Leverett Glacier) became the focus of our third paper together. The approach we adopted combined targeted extraction of plant- and microbial-derived biomarkers with non-targeted

NMR experiments to determine the composition and sources of the organic matter (Pautler *et al*., 2013).

We found that the cryoconite OM from Arctic Canada and Greenland was more heterogeneous than that from Antarctica, likely because it included inputs from vascular plants and mosses that were absent in Antarctica, in addition to microbially-derived components. This was suggested by the nature of the solvent-extracted alkyl-lipids and sterols, and by the detection of lignin- and Sphagnum-derived phenols. Bulk chemical functional groups were identified using solid-state ^{13}C NMR, and the alkyl/O-alkyl proxy was used to evaluate the degradation state of the OM. Solution-state ^{1}H NMR identified both microbial and plant contributions to the Arctic glacier OM. Solution state ^{1}H NMR analyses of base-soluble extracts from the samples revealed both microbial and plant-derived contributions. However, the Antarctic samples were dominated by microbial proteins and peptides. This was expected, given the lack of higher plants in Antarctica. The important finding, however, was that characteristics of the local environment clearly influence the sources and nature of OM found on glacier surfaces, and likely also the processes by which it is cycled and sequestered within glacier systems. Again, this was consistent with our interpretation of previous results derived from spectrofluorescence analyses.

9.7 Characterising Glacial Organic Matter – Mass Spectrometric Methods

Although we were not involved in the work, I think it is also necessary to recognise the important contribution to the study of glacial organic matter made by the Ph.D. research of Maya Bhatia which was conducted at MIT/Woods Hole (under the supervision of Sarah Das and Liz Kujawinski). Maya Bhatia started her graduate career in my group (Bhatia *et al*., 2010). In this work, carried out on the western margin of the Greenland Ice Sheet, Maya used the technique of Electrospray Ionisation Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (ESI-FT-ICR-MS) and multivariate statistical methods to characterise the DOM present in the subglacial, supraglacial and proglacial regions of the ice sheet. These results were compared with those of analyses of the DOM exported from the ice sheet in subglacial meltwater discharge over the course of a melt season (Fig. 9.9).

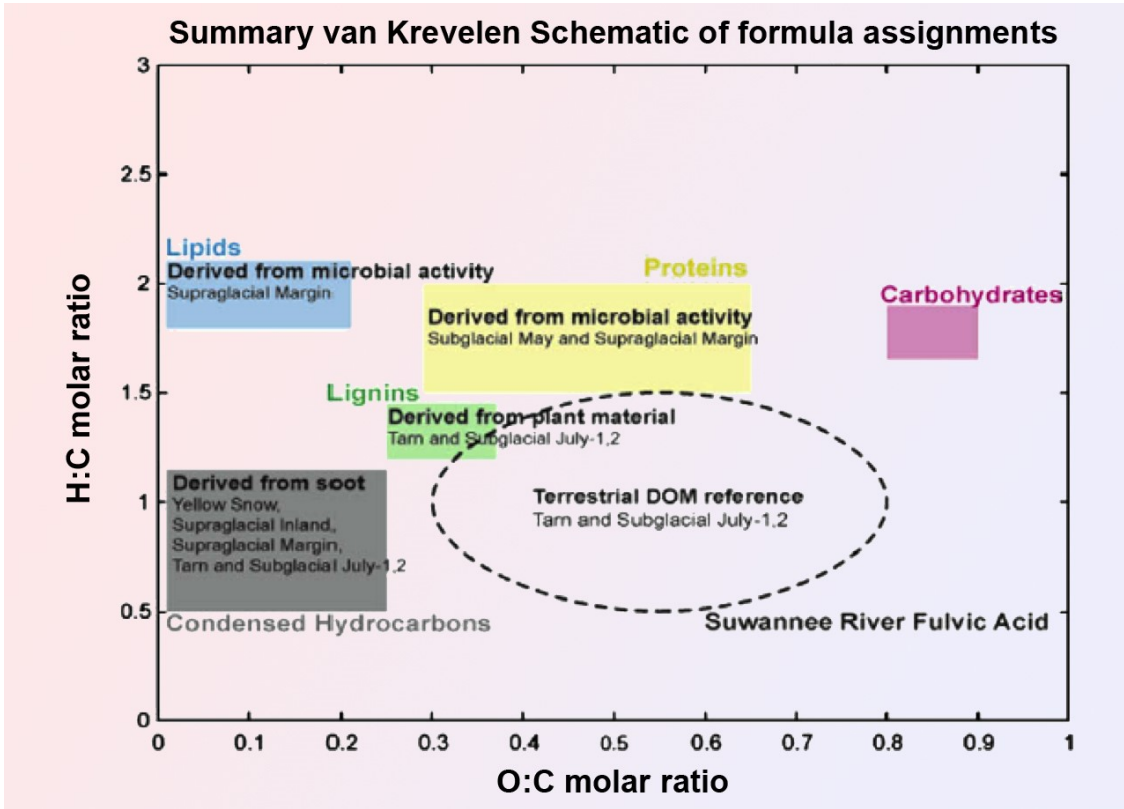

Figure 9.9 Van Krevelen diagram showing the major groups of organic compounds found on the western margin of the Greenland Ice Sheet south of Jakobshavn, and the environments in which they were found (modified from Bhatia *et al*., 2010).

Maya found that the different carbon pools contained different classes of compounds. Protein-like compounds were an important component of supraglacial samples and early melt season subglacial discharge, suggesting production by autochthonous microbial processes on the ice surface. In contrast, late season meltwater runoff contained more lignin-like material that was likely derived from plant matter and organic soil fractions preserved in overridden soils and vegetation beneath the ice sheet. A further DOM component, thought to be derived from soot, was also found in the supraglacial environment, and in some late summer runoff samples. Although the analytical approach was different, these results were broadly consistent with those that we had previously obtained from other systems using fluorescence and NMR spectroscopy. They also suggested that, given sufficient time and appropriate conditions, microbial communities could oxidise terrestrial organic matter in subglacial environments. This provided further motivation for studying the carbon (and associated nutrient) cycles in glacial systems.

9.8 Subglacial Biogeochemical Weathering and its Impact on Nutrient Fluxes

Our early models for chemical weathering processes in glaciers, initially based on observations at Haut Glacier d'Arolla (but extended as we obtained new results from John Evans Glacier and Svalbard) assumed that weathering resulted exclusively from inorganic processes. This perspective became less viable as the evidence for microbial activity and the widespread availability of dissolved (and likely also particulate) organic matter in glacier ice and meltwaters mounted.

Jemma Wadham led the task of synthesising what we knew, and articulated a first model of subglacial biogeochemical weathering (Wadham *et al.*, 2010). In part, this was also a first attempt to think about whether, and how, weathering systems under the continental ice sheets in Greenland and Antarctica (and by inference also the Pleistocene Ice Sheets of North America and Eurasia) might differ in some respects from the systems we had studied under relatively small alpine and Arctic valley glaciers. Jemma argued that this was indeed likely to be the case.

The paper suggested that, under small valley glaciers, the main weathering process was carbonate dissolution fuelled largely by a mixture of carbonic acid created by the dissolution of carbon dioxide derived from microbial oxidation of subglacial organic matter (contained in material derived from glacially-overridden soils and sediments, or from *in situ* microbial production), and sulphuric acid derived from sulphide oxidation. Under large ice sheets, however, meltwater residence times were likely to be much longer, and meltwaters were likely to be isolated from sources of atmospheric oxygen for much longer periods of time. These conditions would tend to lead to anoxia and an increase in rates of silicate mineral dissolution relative to the rate of carbonate dissolution. Two other significant conclusions from this paper were that solute fluxes from large ice sheets were likely to be comparable to those associated with the largest rivers on Earth, and that chemical weathering rates in glaciated terrain tend to be very high for a given specific discharge. In effect, the paper made the case that ice sheets likely play a significant role in biogeochemical cycles at the global scale. Given that ice sheets have been much more extensive than they are today at various times in Earth History, it was implicit that there were grounds for exploring how these ice extent changes might have impacted biogeochemical cycling at the global scale.

Two lines of research spun off from this synthesis – studies that investigated the cycling of organic carbon in glacial systems, and studies that attempted to quantify fluxes of biogeochemically significant elements to the ocean from the Greenland Ice Sheet. As previously mentioned, we had been thinking about the possibility of organic carbon cycling beneath glaciers since we first discovered there were microbes at the bed of Haut Glacier

d'Arolla. In part this was because we realised that the last great ice sheets in the northern hemisphere had formed and flowed over areas that, during the present interglacial, store large amounts (currently some 400 x 10^{15} g) of organic carbon in the landscape. It seemed at least plausible that similar carbon stores might have existed in these same areas during previous interglacials, and that some of this carbon would have survived glacial advances and became sequestered beneath the ice sheets, where it would have been available as a substrate for microbial activity.

We also knew there was a significant discrepancy between estimates of the change in terrestrial carbon storage that occurred between interglacial and glacial periods that were based on palaeo-vegetation reconstructions and on analyses of the $\delta^{13}C$ of carbon in the ocean (Adams *et al*., 1990; Van Campo *et al*., 1993). It seemed possible that this discrepancy might be explained if there was a substantial reservoir of organic carbon beneath the Pleistocene ice sheets which was not accounted for in these estimates (*i.e*. this carbon was assumed to be in the ocean, but it was actually still on land). We also thought there was already some evidence for active subglacial cycling of this carbon from gas content measurements from the basal ice layers of the GRIP and GISP2 ice cores in Greenland, which showed very high concentrations of both carbon dioxide and methane (Souchez *et al*., 1995). Most notably, the results from the Greenland ice cores showed that the methane in the basal ice had $\delta^{13}C$ isotope values that suggested a biogenic origin for the methane (Souchez *et al*., 1995; Miteva *et al*., 2009).

Whilst working at John Evans Glacier, I continued to be interested in basal ice and often spent time exploring the glacier margin looking for new exposures of it. This is when I first encountered what we came to call "stinky mud". This was associated with basal ice that contained consolidated fine-grained sediment that gave off a pungent aroma when exposed by melting at the glacier surface. Typically, this sediment contained visible organic matter and I assumed that it was anoxic decay of this organic matter that was generating the characteristic smell. I thought the sediment probably originated in small ice marginal lakes and ponds that could easily be overridden by the glacier and incorporated into the basal ice layer during even small advances. Subsequently, I found something very similar (again detectable by smell) at the termini of the Lower Wright Glacier (where the organic matter came from the foreset sequence of a glacially-overridden delta), at the Suess Glacier in the McMurdo Dry Valleys, and at the margins of the Devon Ice Cap in Arctic Canada. Colleagues who came across it at these sites have also found it in other places they have worked. We all think it provides evidence of active degradation of organic carbon at glacier beds, though we still don't know what gas creates the distinctive smell.

9.9 Ancient DNA in Basal Ice from the Greenland Ice Sheet

In 2007, I had a chance to approach this problem from a different angle. Danish scientist, Eske Willerslev, was interested to see if it was possible to investigate the nature of interglacial landscapes in Greenland by studying the ancient DNA in the basal ice from deep ice cores. He had tried this unsuccessfully with the basal ice from the GRIP ice core but wanted to try again with ice from Dye 3. However, he also wanted to look at some basal ice from a smaller, younger glacier to see if it was possible to recover DNA from this material and, if it was, to determine whether the make-up of any plant DNA he recovered was consistent with the plants that were found in the landscape around the glacier. I was able to provide him with samples from John Evans Glacier to do this, and the results of those analyses showed both good preservation of organic matter, and that the DNA record from the basal ice was a good match to today's local vegetation (Willersley *et al*., 2007).

By contrast, the DNA from the Dye 3 basal ice indicated a vegetation cover very different from that of Greenland today. It included DNA from several tree species – alder, spruce, pine and members of the yew family – an assemblage indicative of a northern Boreal Forest ecosystem – and also a range of herbaceous species that suggested the forest may have been rather open in character. Four different dating methods suggested that this forest ecosystem likely pre-dated the last interglacial period, although precise dating was not possible. Regardless, these results suggested that overridden organic matter could be preserved beneath a large ice sheet. It was therefore implicit that if subglacial thermal and hydrological conditions were, or became, suitable, that such organic matter could be a substrate for microbial respiration and a potential source of greenhouse gas production.

I was back to the idea of a "subglacial composter", and this time I felt compelled to pursue it more seriously. To do this, I turned to Jemma Wadham, who I had known since she was an undergraduate in Cambridge, and who was now an academic at Bristol, where she had set up the LowTEX laboratory focused on glacier biogeochemistry. At that time, Ashley Dubnick had started to work in my lab, and she had begun her work on characterising organic matter from basal ice using spectrofluorescence methods. She seemed like the perfect candidate to send to LowTEX to work with Jemma's group on a study of methanogenesis in basal ice and subglacial sediments. So, off she went with a collection of samples from Antarctica and Ellesmere Island, to which Jemma added some more samples from Norway and Greenland. My original intent was for Ashley to run some long-term incubations of her (deliberately organic-rich) samples to see if it was possible to generate methane from them. However, the talent pool and facilities in Bristol were such that the project became much bigger

than that. We were also able to characterise and measure the abundance of organic matter in the samples from each location, and determine the abundance, diversity and activity of methanogenic archaea in each sample. Marek Stibal led the publication of these results (Stibel *et al*., 2012).

In short, the sample sets from Lower Wright Glacier, John Evans Glacier (both containing lacustrine sediment), and Russell Glacier (soil material)) contained significant (up to 7 x 10^4 cells g^{-1}) numbers of methanogens. Clone libraries from both Lower Wright and John Evans Glaciers contained clones of *Methanomicrobiales* and *Methanosarcinales,* while the Russell Glacier sediment contained only clones of hydrogenotrophic *Methanomicrobiales.* Incubations were conducted for 600 days, and it took up to >200 days for methane to be measured. Rates of methane production varied greatly between the different samples, ranging from 10^1-10^5 fmol g^{-1} d^{-1} depending on the origin of the sediment and the character of the organic carbon it contained. This suggested that we might anticipate similar variability in methane production rates beneath glaciers and ice sheets as a function of the nature and carbon content of the subglacial substrate.

Interestingly, Eric Boyd and Mark Skidmore (2010), working at one of my old stomping grounds, Robertson Glacier in the Alberta Rocky Mountains, had also found evidence of active subglacial methanogenesis, this time involving euryarchaea of the order *Methanosarcinales.* Porewater methane concentrations in their two subglacial sediment cores reached 16-29 ppmv, and methane was produced in enrichment cultures when these sediments were incubated at 4 °C (Boyd *et al*., 2010). This study also reported evidence that methanotrophic archaea might be present in the Robertson Glacier subglacial environment.

Subsequently, Markus Dieser and colleagues (2014), working at Russell Glacier in Greenland, produced evidence for the existence and activity of methanotrophs beneath the glacier margin, as well as for subglacial microbial methane production (Dieser *et al*., 2014). Along similar lines, a 2017 study of methane cycling in subglacial Lake Whillans in West Antarctica (led by Alexander Michaud; Michaud *et al*., 2017) found evidence of both hydrogenotrophic methanogenesis and aerobic methanotrophy, and concluded that most of the methane produced in the lake sediments was converted to carbon dioxide and biomass before it had any opportunity to reach the atmosphere.

Together these four studies, along with the earlier ice core evidence, provided a strong indication that active methane cycling does occur in subglacial settings, with microbial populations in well oxygenated subglacial meltwaters perhaps acting as a significant sink for methane. If this turns out to be generally the case, then it would negate suggestions that subglacial methanogenesis might result in significant reservoirs of methane in subglacial

sediments (Wadham *et al*., 2012) that could be released to the atmosphere during and after periods of deglaciation (as had been suggested by Wadham *et al*., 2013).

It remains to be seen whether subglacial lakes and subglacial meltwater channels located close to an ice sheet margin are fully representative of the range of subglacial environments in which biogeochemical cycling of carbon dioxide and methane take place. Indeed, the high methane concentrations found in the basal ice from GRIP and GISP2 suggest that methanotrophy may be limited in the deep interior regions of large ice sheets. Regardless, subglacial methane oxidation would result in the production of carbon dioxide which, if stored subglacially, could also escape to the atmosphere during deglaciation with potential impacts on climate. Furthermore, when dissolved in water, this carbon dioxide would produce carbonic acid, which is a major driver of subglacial mineral weathering.

Recently, Jon Telling and others (Telling *et al*., 2015) raised the question of how subglacial microbial populations that were dependent on organic carbon as an energy source could survive in the long term, given that subglacial carbon reservoirs would be progressively depleted over time, removing the energy source on which these populations depend. They argued, on the basis of experimental evidence, that one possible alternative source of energy was H_2 produced abiogenically during subglacial comminution of bedrock. This mechanism of H_2 production involves the reaction of water with mineral surface silica radicals formed during bedrock comminution. This process might be a means of supporting microbial life and biodiversity in subglacial environments throughout extended and extensive glaciations such as those that occurred during the Neoproterozoic.

9.10 Nutrient Biogeochemistry and Export to the Oceans

Given the evidence for active microbial populations in subglacial environments and their involvement in bedrock weathering and carbon cycling, it is likely that other nutrient elements, such as silica, nitrogen, phosphorous, sulphur, iron, and manganese, are also being actively cycled in glacial environments, and that the products of this cycling are exported in meltwater runoff and/or icebergs to downstream fluvial, lacustrine, and marine environments. The evidence that sulphide oxidation is an important weathering process and a significant source of protons that are consumed in subglacial weathering reactions confirms this for iron and sulphur.

However, much less is known about the cycling of the other nutrient elements. Much of the work done to date has focused on computing fluxes of these elements from land ice to the ocean, comparing these fluxes with those measured from major river systems, and

considering how nutrient export from ice sheets might impact productivity in environments beyond the ice sheets - in particular the marine environment (*e.g.*, Wadham *et al.*, 2013). The existence of measurable fluxes confirms that cycling is taking place, but the precise locations where this is happening, the conditions under which it occurs, and the processes involved are less well understood. However, understanding is increasing rapidly as more researchers are attracted to the field and new studies are published.

In the oceans, nutrients exported in meltwater may affect nearshore productivity, as evidenced by the co-occurrence of phytoplankton blooms with areas of the ocean where meltwater inputs deliver nutrients both in the dissolved phase and in association with suspended sediments. By contrast, icebergs may play an important role in the supply of nutrients, in particular iron, to the ocean interior (especially around Antarctica). Iron exported in icebergs is typically in the form of iron (oxyhydr)oxide nanoparticles derived from subglacial weathering of reactive, iron-bearing mineral phases like sulphides, carbonates, olivines, and pyroxenes (Raiswell *et al.*, 2006). These nanoparticles are released into the ocean slowly over time as the basal portion of the icebergs melts. Fluxes of Fe to the oceans in meltwater from the Greenland and Antarctic Ice Sheets are of interest because coastal ocean around these ice sheets are very productive, but in some areas (like Greenland) iron-limited.

Jon Hawkings and others (2014) used measurements of Fe concentrations in west Greenland (Leverett Glacier) subglacial runoff as a basis for estimates of bioavailable Fe fluxes to the ocean of 0.40–2.54 Tg per year in Greenland and 0.06–0.17 Tg per year in Antarctica. These fluxes are dominated by a nanoparticulate suspended sediment fraction that is highly reactive and potentially bioavailable. They are comparable in magnitude to fluxes associated with aeolian dust inputs to the oceans surrounding the 2 great ice sheets, and likely to increase if ice sheet melt and runoff increase in a warming climate.

Rock flour in glacial runoff is a significant source of Fe (II) and Fe (III) to the polar waters that surround Greenland. This particulate flux of Fe exceeds the dissolved phase Fe flux in Greenland glacial meltwaters (Hopwood *et al.*, 2014), and some fraction of it appears to be bioavailable. It may impact the biota in the so-called “High nutrient, low chlorophyll (HNLC)” zones in the oceans around Greenland. However, the labile fraction of dissolved Fe varies significantly between different Greenlandic rock flours, and the fluxes are not directly proportional to the total Fe export. Productivity in ocean waters around Greenland tends to be Fe-limited, and there have been suggestions that it could be stimulated by increased fluxes of meltwater and Fe from the ice sheet. However, it appears that processes within Greenland fjords may remove Fe from surface waters before it can be exported to coastal seas around Greenland (Hopwood *et al.*, 2016). In addition, the physical circulation in the oceans around

Greenland is apparently not very effective at exporting Fe into offshore waters in the North Atlantic. Hence, glacial runoff from Greenland is not a major source of Fe to the North Atlantic Ocean as a whole (Hopwood *et al*., 2015).

Other examples of studies of nutrient fluxes in meltwater led by Jon Hawkings include two that address exports of additional nutrient elements from the Leverett Glacier (Table 9.1). In their initial paper, Hawkings *et al*. (2015) documented dissolved phase fluxes of phosphorus, nitrogen, and silica, based on 4 years of monitoring data from the glacier's outflow stream. Note, however, that these fluxes were, in part, computed on the basis of near-continuous measurements of the electrical conductivity (EC) of the meltwaters, using correlations between nutrient element concentrations and the EC of the meltwaters at the time of sampling. The monitoring period included 2010 and 2012, the two highest runoff years on record in West Greenland. As expected, fluxes peaked in the highest runoff years. Nutrient fluxes were dominated by labile particulate macronutrients, which accounted for 50 % of nitrogen exports and 80 % of silica and phosphorous exports. Fluxes are likely to increase over time as melt runoff from the Greenland Ice Sheet is predicted to continue to increase in a warming climate.

Table 9.1 Computed fluxes of water, total solute, sediment, and dissolved and exchangeable nutrient elements from the Leverett Glacier, West Greenland, 2009-2012 (from Hawkings *et al*., 2015).

	Units	Year			
		2009	2010	2011	2012
Greenland Ice Sheet runoff *	km^3	348	559	466	665
Leverett Glacier discharge	km^3	0.94	1.79	1.10	2.03
Snowline above catchment	est. days	45	100	73	85
Snowline retreat from margin	km	125	135	135	149
Solute Flux	eq	3.0×10^8	5.6×10^8	3.2×10^8	5.6×10^8
Sediment Flux	t	3.7×10^6	2.6×10^6	3.0×10^6	2.2×10^6
Dissolved inorganic nitrogen †	t	25	46	26	48
Dissolved silica †	t	130	230	120	230
Dissolved inorganic phosphorus†	t	6.2	12	6.7	12
Dissolved inorganic nitrogen ‡	t	22	41	25	47
Dissolved silica ‡	t	110	220	130	240
Dissolved inorganic phosphorus‡	t	7.8	15	8.9	16
Exchangeable NH_4**	t	19-58	13-41	15-47	11-35
Amorphous silica**	t	18,000-44,000	12,000-31,000	14,000-36,000	11,000-26,000
NaOH extractable phosphorus**	t	20-130	14-92	16-110	12-78

All estimates are shown to Decimal Day 230/231, i.e. 17 August.
Estimates are reported with 2 significant digits.
eq = molar equivalent
t = tons of dry element
Snowline: the boundary where snow covers the underlying ice. Down glacier from this point is exposed ice, where the snow cover has melted.
* Greenland Ice Sheet runoff estimates from Tedesco *et al.* (2013).
** Sediment fluxes given as range based on minimum and maximum extractable nutrient concentrations.
† Fluxes estimated with electrical conductivity.
‡ Fluxes estimated using discharge weighted mean.

Putting these results into a broader context, Hawkings *et al.* (2016) showed that concentrations of soluble reactive P in ice sheet meltwaters (up to 0.35 µM) are comparable to those found in major Arctic rivers, resulting in specific yields of 17-27 kg P km^{-2} yr^{-1}. These are among the highest reported in the literature. Total P yields computed for Greenland on the basis of these limited data exceed riverine values reported in the literature by an order of magnitude, and (if correct) may make the Greenland Ice Sheet the dominant source of total P input to the Arctic oceans. Most of this export occurs in particulate form, however, and it is not known how much becomes buried in (or re-suspended from) coastal and fjord sediments. Furthermore, the bioavailability of particulate phase nutrients may be limited, and this could restrict their impact on the productivity of glacially-influenced marine waters (Hodson *et al.*, 2004).

With respect to dissolved silica, Meire *et al*. (2016) working in Greenland fjord systems reported that the export of dissolved Si in glacial runoff is high relative to that of other macro-nutrient elements. They estimated a total annual flux from Greenland of 22 +/10 Gmol Si yr^{-1}, and noted that this input to the ocean around Greenland seems to favour the productivity of diatoms relative to other phytoplankton taxa. However, the impact on total productivity is limited by low nitrate concentrations in the fjord waters.

9.11 Nutrient Cycling in Glacial Systems

To date there have been few studies of the cycling of specific nutrients in glacial systems. However, some of the most comprehensive studies have involved scientists who worked in our groups – Andy Hodson, Jon Telling, and Ashley Dubnick – so I will use their work to provide examples of what we know. Andy's work, with his Ph.D. student Peter Wynn, was focused on the nitrogen cycle at polythermal Midtre Lovenbreen in Svalbard (Wynn *et al*., 2007). Jon's work focused on supraglacial nitrogen cycling by microbes on the Greenland Ice Sheet (Telling *et al*., 2012), and Ashley's (carried out on the cold-based Joyce Glacier in the McMurdo Dry Valleys with Jemma Wadham and John Orwin) addressed supraglacial and proglacial nutrient cycling in an environment where there is no subglacial meltwater drainage (Dubnick *et al*., 2017).

Wynn and Hodson's paper (Wynn *et al*., 2007) relies upon analyses of major ion chemistry and natural environmental isotopes of nitrate and ammonium to track the processes involved in subglacial nitrogen cycling. Measured nitrate fluxes in subglacial runoff were higher than could be explained simply by the melt-induced release by melting of the nitrate contained in the supraglacial snowpack and glacier ice. This suggested that additional nitrate was being supplied to runoff by processes active at the glacier bed. The $\delta^{18}O$ composition of the excess nitrate suggested it had a microbial origin, while its $\delta^{15}N$ values were higher than those found in the supraglacial runoff. The authors considered three possible processes that might explain these observations: nitrification of supraglacially-derived ammonium, mineralisation of organic N, and dissolution of geologically-derived ammonium.

Based on analyses of the mass fluxes of nitrogen compounds in the subglacial meltwater stream at Midtre Lovenbreen and their $\delta^{15}N$ values, it was concluded that much (but not all) of the excess nitrate could be attributed to nitrification of supraglacially-derived ammonium at the glacier bed. Mineralisation of organic nitrogen was thought to account for the residual nitrate (though some contribution from dissolution of ammonium contained in bedrock could not be ruled out – though it would have required large isotopic fractionation effects to have occurred during dissolution). However, the measured loss of ammonium from

the glacier surface exceeded what could be accounted for by the nitrate excess in runoff at the glacier terminus. This suggests that some of the NH_4^+ was assimilated into organic matter in other microbial habitats, and implies that the cycling of nitrogen in glacial environments may be non-conservative. Needless to say, these results clearly imply active nitrogen cycling within this glacial environment.

Jon Telling's work in Greenland was carried out along a 79 km long transect up the Leverett Glacier and onto the Greenland Ice Sheet. He found that, within 7.5 km of the glacier terminus, dissolved nitrate was depleted and ammonium was produced within cryoconite holes on the glacier surface. This seemed to imply that microbial uptake of nitrate and ammonification were taking place. *In situ* acetylene assays detected N-fixation within a 100 m wide debris-covered zone at the glacier margin and up to 5.7 km inland. It is therefore presumably important for the microbial communities in this localised region but not of great significance in the context of the ice sheet as a whole.

Since all the runoff from Joyce Glacier follows a surface drainage pathway, Ashley Dubnick adopted the approach of following the water along this pathway from the up-glacier limit of melting on the glacier surface, through the ice marginal zone *via* a series of gullies on the glacier's terminal slope and a small proglacial pond, to enter the Holland Stream, which drains into extraglacial Lake Colleen. From there it continues its journey to the margins of the Garwood Glacier. Ashley identified 11 distinct supraglacial, ice-marginal, and proglacial hydrological units along this drainage pathway. These were differentiated in terms of their water sources (snow, ice, sediment pore water), meltwater residence times, hydrologic connectivity, and access to allochthonous and autochthonous sources of sediment and nutrients. The downstream sections of the stream were especially nutrient-poor.

Ashley investigated how the passage of water through this system affected the concentrations of dissolved inorganic nitrogen and phosphorus, and of specific fractions of DOM in the runoff (Fig. 9.10). She found that snow and glacier ice were sources of nitrate and ammonium respectively, and that cryoconite holes, ice-covered cryolakes and streams on the glacier surface were sinks for each of these nutrients. The cryoconite holes and cryolakes were also a source of a protein-like component of DOM, for which the supraglacial streams were a sink. As the waters drained through the ice-marginal zone, they picked up phosphate from a variety of ice types (some of which contained rock debris) and from flow through the ice marginal gullies and a small proglacial pond that was affected by ice avalanching from the marginal ice cliff. They also acquired nitrate from this pond and the ice marginal gullies, and ammonium from the ice margin gullies and contact with basal debris-bearing ice. A second distinctive component of DOM was added as a result of flow through the pond. Drainage from

the pond into the upstream section of the proglacial stream resulted in decreases in the concentrations of phosphate, nitrate, and ammonium.

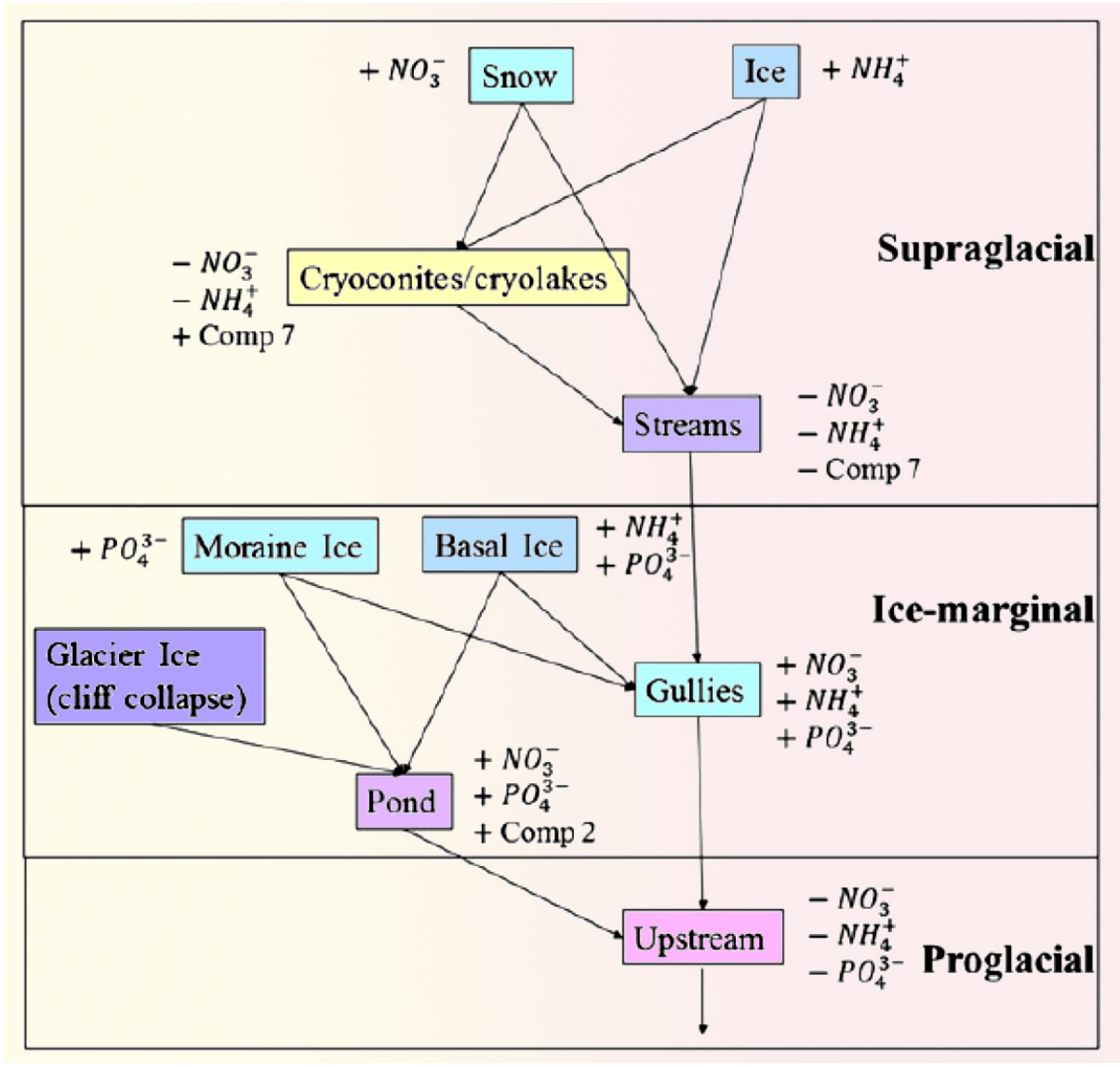

Figure 9.10 Summary of the sources and sinks for organic and inorganic nutrients in the supraglacial, ice margin, and proglacial environments of the Joyce Glacier System, McMurdo Dry Valleys, Antarctica. Arrows indicate flow pathways, "+" indicates sources, and "-" indicates sinks for nutrients (modified from Dubnick *et al*., 2017).

Typically, dissolved phase concentrations in the stream decreased as discharge increased, resulting in a relatively constant flux (or trickle) of most nutrients to the downstream environments. By contrast, concentrations of dissolved inorganic nitrogen increased with discharge, resulting in pulsed delivery (or treats) of this nutrient to downstream environments. DOM concentrations were not clearly related to discharge, but were nonetheless highly

variable. Thus, delivery to downstream environments was also pulsed but not synchronised with that of dissolved inorganic nitrogen. The implications of these behaviours for stream ecology have yet to be explored.

Together, these two studies demonstrate that there is detectable cycling of nutrient elements in glacial systems and that this is not confined to subglacial environments where access to sediment and soil materials is presumably maximised. There is, however, still a lot to be learned before we will fully understand how the different nutrient cycles are coupled in these systems, and studies that incorporate the role of the gaseous phase in the transformations of organic matter that take place in glacial systems have barely started (although there has been a reasonable amount of speculation about this, to which we must confess to contributing).

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10. LIFE IN SUBGLACIAL LAKES (MT)

Both Martin Siegert and John Priscu had a huge desire to access and directly sample subglacial lakes in Antarctica (Priscu *et al*., 2003). Martin Siegert painstakingly put together the case to sample subglacial lakes (Siegert *et al*., 2007, 2012), both for the palaeo-climate information they might contain at ice divides in particular, and to ascertain whether microbial life existed in what might be thought of as the most inhospitable environment on the planet, given the temperature, pressure and lack of light. He funded the Subglacial Lake Ellsworth (SLE) project *via* a NERC Large Grant, with the British Antarctic Survey (BAS) as one of the key project partners. The principal roles of BAS were to provide the logistics and project management, and to drill the hole near the ice divide of the West Antarctic Ice Sheet in the vicinity of the Ellsworth Mountains. Matt Mowlem (NOC, Southampton) was tasked with designing and building a measurement and sampling probe, Mike Bentley (Durham) and Dom Hodgson (BAS) were to be the sediment corers, John Parnell (Aberdeen) was in charge of organics, David Pearce (then BAS, now Northumberland University) was in charge of microbiology, and Jemma Wadham and I were in charge of the hydrochemistry.

Meanwhile, John Priscu, along with Ross Powell and Slawek Tulaczyk, pioneered WISSARD (Whillans Ice Stream Scientific Access Research Drilling) (Priscu *et al*., 2010), which was funded by the NSF. WISSARD was located over Subglacial Lake Whillans (SLW) near to the grounding line of the Whillans Ice Stream, which feeds into the Ross Ice Shelf (Fig. 10.1). The ice thickness here was about 800 m, whereas it was ~3 km over SLE. WISSARD benefitted from relatively close proximity to McMurdo Station, unlike SLE which was almost half a continent away from the BAS base at Rothera.

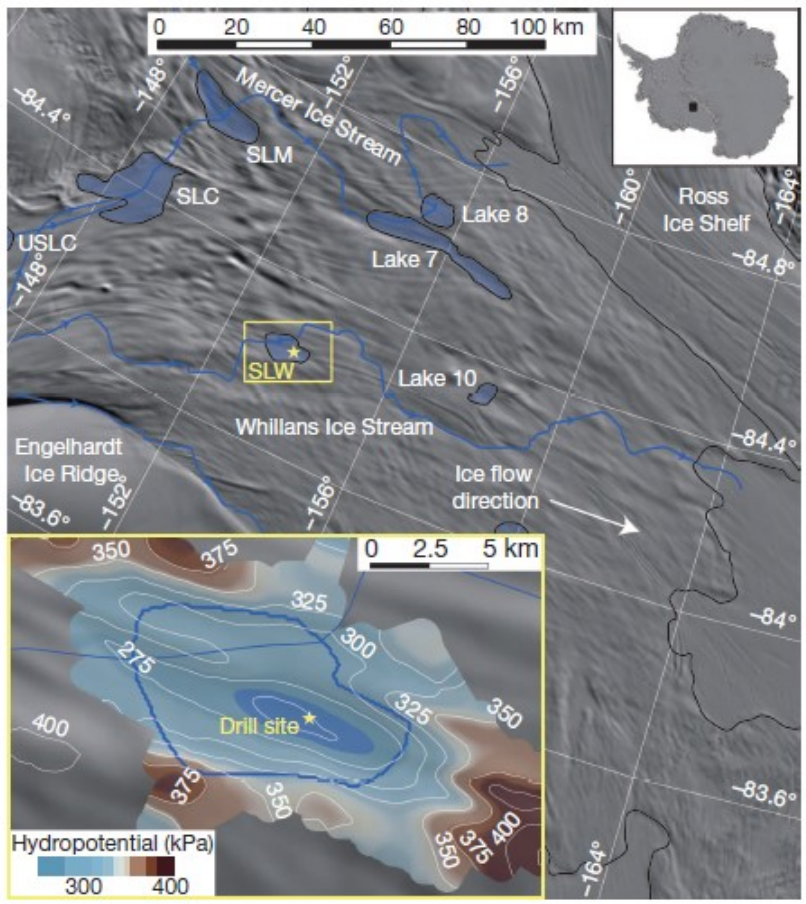

Figure 10.1 Location, dimensions and hydropotential of Subglacial Lake Whillans (SLW) (from Christner *et al*., 2014, with permission from Nature Publishing Group).

There was good interaction between the groups, and we were very open with each other about the methods that we were employing. For example, we exchanged much information about sterilisation and filtration methodologies. These were essential if the water and sediment we were attempting to collect should contain microbes. We had to demonstrate conclusively that we had not introduced the microbes we hoped to collect, and we had a responsibility to ensure that we did not contaminate the lakes. There were very different sampling strategies, since the thinner ice above SLW allowed a wider hole to be drilled, allowing standard oceanographic Niskin bottles to be employed (Tulaczyk *et al*., 2014), whereas the narrower, deeper hole above SLE required Matt to design a very elegant, bespoke water sampler, CTD (conductivity, temperature and depth probe), and short sediment corer, all the width of a standard compact disk (Mowlem *et al*., 2016).

The SLE drilling did not go well, which was a tragedy for all involved. I was impressed with the dignity and effort shown by the field team. They couldn't have worked any harder or smarter.

The technology was just not up to such a demanding task in such a remote location. We abandoned field work in late December 2012, and WISSARD deployed shortly afterwards. WISSARD had a very experienced field and drilling team, and were successful in penetrating the lake. Even so, several adverse circumstances limited their safe, contamination-free sampling of the lake to a window of tens of hours only. They worked flat out to obtain enough water and sediment to produce one of the landmark papers in subglacial lake research – the first waters and sediments sampled directly from a subglacial lake, albeit a small and shallow subglacial lake, showed clear evidence of microbial life (Christner *et al*., 2014). The adage that “wherever there is water, there is life” near the earth surface was apt yet again, and the odd kilometre or so of ice above the water, the lack of light and the low temperatures (-0,5 ^{o}C) were no impediments to the persistence of a microbial ecosystem.

10.1 Microbial life in Subglacial Lake Whillans

Microbes were found in the water column (Fig. 10.2), at concentrations of ~10^5 cells per mL, almost three orders of magnitude higher than in the borehole waters. Microbes were also found extensively in the lake sediment. Both bacteria and archaea, heterotrophs and autotrophs were found, and the microbial ecosystem appeared to be chemosynthetically driven. Many of the phylotypes of the microbes were closely related to chemolitho-autotrophic species that use reduced N, S and Fe compounds as energy sources. Rate experiments showed that chemoautotrophic production was sufficient to support heterotrophic metabolism in the lake (Christner *et al*., 2014).

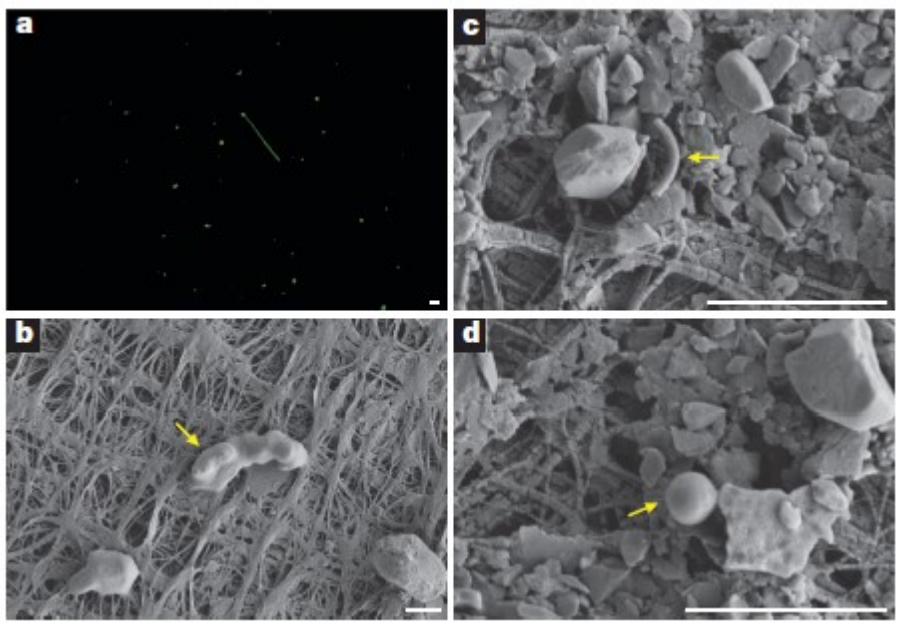

Figure 10.2 Morphological diversity of cells in Subglacial Lake Whillans: **(a)** epifluorescence micrograph; yellow arrow indicates **(b)** cells with rod; **(c)** curved rod cell; and **(d)** coccoid cell. The scale bar is 2 μm (from Christner *et al*., 2014, with permission from Nature Publishing Group).

The water chemistry was particularly revealing about microbial processes. The oxygen saturation was 16 % of surface water concentrations at -0.5 ºC. DIP concentrations were ~3.1 μmol L^{-1}, and the predominant DIN species was NH_4^+ (~2.4 μmol L^{-1}). The DIN:DIP molar ratio was ~1.1, suggesting that N was the limiting nutrient. The molar ratio of N:P in the particulate matter in the water column was about 15 times that of the active microbial population, consistent with N being the limiting nutrient, and there being tight cycling of N in the ecosystem. The most abundant operational taxonomic units (13 % of the sequence data) of microbes in the lake water were closely related to the nitrite oxidising betaproteobacterium, *'Candidatus* Nitrotoga arctica (Alawi *et al*., 2007). The DOC concentration was ~220 μmol L^{-1}, and acetate and formate concentrations were ~1 μmol L^{-1}, illustrating that a proportion of the DOC is labile, again suggesting that there was turnover of the microbial organic C pool (Christner *et al*., 2014).

The solute in the lake water (Table 10.1) consisted of about 0.6 % seawater, consistent with the sediment being marine, dating from before the ice sheet grew. The remaining non-sea salt solute was of Na^+-HCO_3^--Ca^{2+}-SO_4^{2-}, similar to that found previously from waters extracted from beneath the Kamb Ice Stream (Skidmore *et al*., 2010). Carbonation of silicates and sulphide oxidation were invoked as the principal weathering reactions, and the locus of the biogeochemical weathering reactions was felt to be in the fine-grained sediment in the lake floor, where pore water concentrations were much higher than concentrations in the lake waters, implying that solute diffused out of the sediment into the lake. This idea was explored in greater detail in a subsequent paper (Michaud *et al*., 2016), where ion exchange was felt to be the mechanism that removed Ca^{2+} from the pore waters, relative to that anticipated from sea water concentrations. These observations were similar to those made by Jemma Wadham, based on her work at Finsterwalderbreen (Wadham *et al*., 2000), which suggested that ion exchange occurred in subglacial sediments. Furthermore similar results were found from an analysis of the different chemistries of subglacial meltwaters beneath smaller glaciers and ice sheets, on the basis of which silicate weathering was inferred to become increasingly important under ice sheets (Wadham *et al*., 2010). It has been a very gratifying experience to see all these pieces of work over the years fall into a bigger and more coherent picture as our knowledge base expands. Alex Michaud, who was a graduate student of John Priscu and

Mark Skidmore, also noted that the sea water component of solute in the sediment increased down core, consistent with sea salt and other solute diffusing out of the sediment into the lake water (Michaud *et al*., 2016).

Table 10.1 The average chemical composition of waters in Subglacial Lake Whillans. The solute is partitioned into sea water and non-sea water components, on the basis that all the Cl^- comes from sea salt (Christner *et al*., 2014).

Crustal and seawater components to SLW waters

	μeq L^{-1}							
Sample	Na^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	SO_4^{2-}	HCO_3^-
SLW Average *	5276	186	507	859	31.5	3537	1111	2111
Sea water component †	3038	66	691	132	0.4	3537	366	16
Non-seawater, crustal weathering component ‡	2239	120	-183 §	726	31.1	0	745	2096

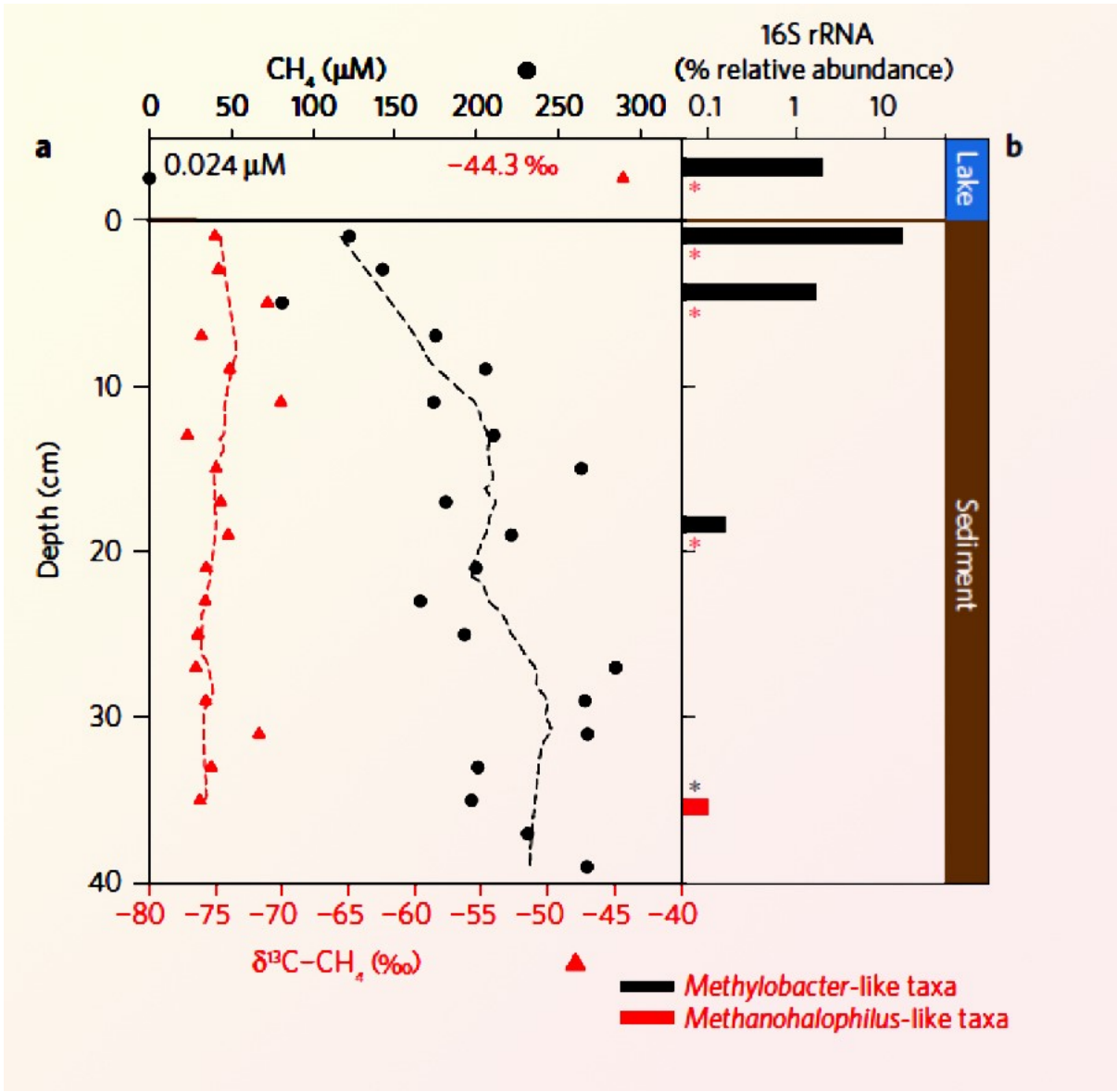

Figure 10.3 Concentration and carbon isotope composition of CH_4 in the sediment beneath Subglacial Lake Whillans. The distribution and relative abundance of methane oxidising and methane producing microbes is also shown (modified from Michaud *et al*., 2017).

Further analysis of the pore waters produced an important discovery. Alex Michaud found that CH_4 was being produced in the sediments beneath Subglacial Lake Whillans (Michaud *et al*., 2017) (Fig. 10.3). Methane producing microbes were found in the deepest part of the short (~40 cm) core, but were absent in the upper core and the water column, where methane oxidising microbes were found. CH_4 in the water column had a $\delta^{13}C$ that showed evidence of oxidation of CH_4 to CO_2, consistent with >99 % of the CH_4 being oxidised in the surface layer of sediment. The δD and $\delta^{13}C$ of the CH_4 indicated that the methane was being produced by CO_2 reduction by H_2 (equation 10.1).

$$CO_2 + 4H_2 \leftrightharpoons CH_4 + 2H_2O \qquad (10.1)$$

The excitement around this observation is that methane oxidation is a potentially significant driver of microbial processes in the surficial sediments and waters beneath the Antarctic Ice Sheet. Indeed, large reservoirs of methane have been predicted to occur in the great thicknesses of former marine sediments under the ice sheet, and the slow seepage of this methane out of the sediments is a legacy energy and carbon source from photosynthesis in times of open marine waters in the past. The even more exciting question relates to where the H_2 comes from. It is my guess that crushing of bedrock by glacier erosion is the source (Telling *et al*., 2015), and that this will be a big research theme in the future (Tranter, 2015).

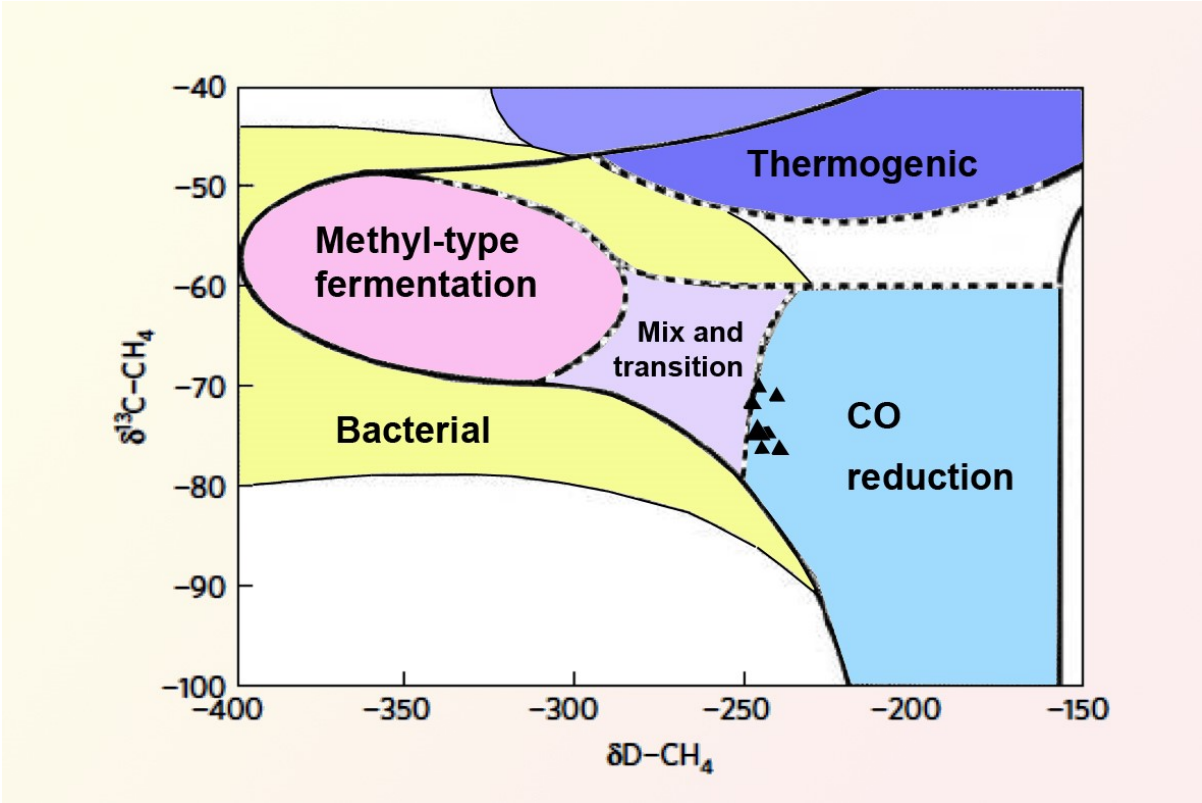

Figure 10.4 Differing mechanisms of CH_4 formation, as differentiated by δD and $\delta^{13}C$ isotopes (modified from Michaud *et al*., 2017).

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11. CONCLUDING REMARKS (MS and MT)

Neither of us can quite believe that the Arolla project could have given rise to the spectrum of work we have described above. We have been fortunate to have worked with so many outstanding post-graduates, post-docs and peers, and we feel that the sum of these efforts is much more significant that anything we have done as individuals. We hope that, collectively, we have brought about a better understanding of the processes that underpin glacier hydrology and glacier hydrochemistry and their role in global scale processes. This in turn has led to an appreciation that microbes play a large role in the biogeochemistry of glacier beds, and that labile Fe species are both a reactant and a reaction product. A full suite of redox reactions can occur at glacier beds, from oxidation of organic matter to methanogenesis. Glacial chemical weathering and microbial processes occur despite the low temperatures and the absence of soils.

We were asked to gaze into the crystal ball and to predict the new areas in our field. Three things stand out. First, glaciers can no longer be ignored in studies of local, regional and global geochemical cycles, particularly if those studies involve the macro- and the micro-nutrients. It seems very clear that modern chemical and biological oceanographers see the need to examine the impact of glacier nutrients on coastal waters and the polar oceans, and to examine the reactivity of glacio-marine sediment, and its potential impact on benthic fluxes. Just how soluble glacier debris is in seawater, and how fast components of the debris dissolve in sea water impacts on the bioavailability of amorphous Si and Fe, for example. These dissolution experiments should also be linked to incubation experiments, conducted with the principal phytoplankton of the polar oceans, so that the release of nutrient and utilisation by phytoplankton can be established, along with the possible need for other macro- and micro-nutrients to maximise productivity.

Second, the production of free radicals on crushed glacier debris has the potential to convert quartz into a material that produces H_2, which can sustain the base of a microbial food chain. This was an unthinkable possibility for glacier geochemists even five years ago. This topic has legs.

Finally, there will be further exploration of the drainage systems and microbially catalysed reactions at ice sheet beds. Both the Antarctic and Greenland Ice Sheets grew over existing sediments, which provide legacy organic matter for the microbes to utilise. The migration of the reaction products, either by diffusion or advection, can drive ecosystem dynamics downstream. The carbon cycle of ice sheets will surely throw up more surprises, as Blood Falls and Subglacial Lake Whillans have both shown.

Another theme may be how widespread deglaciation, driven by global scale warming, will influence the magnitude and composition of nutrient fluxes to the oceans, and what will be the impacts on marine biological productivity and ecology. Furthermore, as melt rates increase, fluxes of stored contaminants from glaciers and ice sheets into downstream aquatic ecosystems are likely to rise in the short term. The ecological consequences of this will merit close attention.

It seems to us that glacier biogeochemistry will continue to grow and excite earth scientists over the coming decades, as more glacier and glacier-influenced environments are sampled, and more information pointing to the reactivity of glacier debris comes to light. We hope that this work remains firmly grounded in good glaciological principles. Richard Alley claimed that "*we're all glaciologists now*", given climate warming and ice melt contributions to sea level rise. We think that modern biogeochemists will make this call too. Good luck!